THE CHEMICAL TECHNOLOGY OF TEXTILE FIBRES

THE CHEMICAL TECHNOLOGY OF TEXTILE FIBRES

THEIR ORIGIN, STRUCTURE, PREPARATION, WASHING,
BLEACHING, DYEING, PRINTING, AND DRESSING

BY

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BY
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PREFACE TO FIRST EDITION

In the present volume, dealing with the Chemical Technology of the Textile Fibres (except as concerns the dyestuffs, which will be treated in a separate work[1]), the author has been obliged to condense the available matter as much as possible, in order to preserve the form of a textbook. Nevertheless, it seemed necessary, in certain cases, in the interests of the book, to give definite data and an exact description of individual processes. In such instances the details have been gathered exclusively either from the author's personal experience or from reliable sources.

The most important part of the book is the chapter treating of dyeing, whilst, on the other hand, the subject of printing had to be dealt with in a more general fashion, the materials being less suitable for treatment in textbook style.

The author thinks it desirable to point out that in the present work an attempt has been made to completely separate the chemical and mechanical technology of the subject, a standpoint he considers justified by the extensive area occupied by each of these branches. Hence only a few sketches of apparatus have been given; and the methods of dressing the finished goods have been described very briefly, since they almost entirely belong to the domain of mechanical technology.

The author is indebted to Prof. J. Zipser for the whole of the sketches given, and to Mr. C. Schimke, teacher of dyeing at the Royal State Trade School, Bielitz, for much assistance in the production of the book.

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[1] *A Textbook of Dye Chemistry* (The Chemistry of Dyestuffs), published by Scott, Greenwood & Son, 8 Broadway, Ludgate, London, E.C. 4, 1920.

PREFACE TO SECOND EDITION

IN this edition the general arrangement and treatment of the subject are on the same lines as in the first, though of course, there have been numerous alterations and additions together with the introduction of new matter, all of which, however, it is hoped, will improve the usefulness of the work.

The principal changes introduced are as follows:—

In Chapter I the sections relating to artificial silk and mercerisation have been enlarged, and particulars of hydrosulphite have been added to the section on bleaching agents.

New features in Chapter II are the practice of wide-open bleaching and the Maertens process of wool scouring.

In Chapter III the question of loading silk has been dealt with more fully.

In Chapter IV the theory of the dyeing process has been entirely re-cast, and new matter introduced including: the application of the sulphur dyes, froth dyeing, and Green's table for the identification of dye-stuffs on the fibre. The sections on dyeing in the hydrosulphite vat, the selection of dye-stuffs for dyeing and machine dyeing have been more or less re-written.

In Chapter V various alterations have been made, especially with regard to discharge printing, brief mention being also made of pile dyeing and the intermittent printing machine.

In addition the whole book has been revised and corrected.

The author is indebted to Prof. G. Ulrich for valuable assistance in connection with the subjects of mercerisation, selection of dye-stuffs, discharge printing, etc., and to Mr. K. Schimke for aid in revising the text.

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CHAPTER I

THE TEXTILE FIBRES

THE name textile fibres applies to such structures as, in consequence of their physical properties, are capable of being spun and worked up into textile fabrics. These fibres are supplied by all three natural kingdoms, and a few of them are also prepared artificially.

Although nearly a thousand textile fibres are known, only a few of them are of real interest. These are cotton, wool, and silk, followed by flax, jute, ramie, and hemp, in a minor degree.

They are divided into four groups:

1. Artificial fibres.
2. Mineral fibres.
3. Vegetable fibres.
4. Animal fibres.

1. ARTIFICIAL FIBRES.

To this series belong spun glass, metal thread, slag wool, and artificial silk.

Spun Glass.—When a glass rod is heated in the flame until perfectly soft, it can be drawn out in the form of very fine threads, which are used to a small extent in the production of very handsome silky fabrics (cravats, etc.). As spun glass can also be produced from coloured glass, the same method can be applied to the production of coloured fabrics. In consequence, however, of the low elasticity of these products, their practical value is nil.

For many chemical purposes, *e.g.* as filtering material for strongly acid liquids, a curly kind of glass wool is produced by drawing out two glass rods of different degrees of hard a capillary double thread. On cooling, these curl up in consequence of the different construction of the two constituent threads.

Metallic Threads. From time immemorial fine golden-silver threads, as well as silver-gilt and silver threads or copper wires, have been used for decorating particularly rich fabrics. Thus the so-called Cyprian gold thread, so renowned for its beauty and permanence in the Middle Ages, is now produced by covering flax or hemp threads with a gilt skin.

Slag Wool. Molten slag is run into a pan fitted with a steam injector, which blows the slag into fibre and furnishes a product which is used to a small extent as a packing material.

Peat yarns have latterly been employed for weaving curtains, bedcovers, etc.

Xylolin, Silvalin, Licella Yarn. Under these names there have appeared on the market, in recent years, yarns and coarse fabrics made of wood pulp, and to some extent of coloured paper. These articles do not play any prominent part in the textile industry, but in order to indicate the manner in which such materials can be converted into yarn, it may be mentioned that a web or fleece is formed in the paper-making machine and divided into narrow strips which are twisted into yarn in the wet state.[1]

Artificial Silk. This product, which is the most interesting of all the artificial fibres, will be described along with Cellulose.

2. MINERAL FIBRES.

To these belong **Asbestos**. This is a decomposition product of serpentine, and is, chemically speaking, a silicate of magnesium and lime, containing in addition iron and alumina. It is found in Savoy, the Pyrenees, Corsica, Mount St. Gothard, etc., and large deposits have also been discovered in northern Italy and Canada.

Asbestos forms long, white, glassy fibres, some kinds, how-

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[1] *Translator's Note.*—Owing to the scarcity of ordinary textile materials in Germany during the war, many articles of clothing, bags (including sand-[illegible]., have been woven from paper yarns.

[illegible], *e.g.* Canadian, are somewhat curly. Alone it is difficult to spin, and is therefore mixed with a little cotton, which is subsequently got rid of by heating the finished fabric to incandescence. Asbestos fabrics of this kind are generally used where exposure to high temperature is necessary, *e.g.* for packing steam cylinders and hot machine parts, also as a fireproof material in the manufacture of numerous theatrical requisites, etc. Asbestos is difficult to dye. For this purpose the albumen dyes and substantive dyes are used.

3. VEGETABLE FIBRES.

These are supplied in large numbers by the vegetable kingdom. They are divided into three classes: (*a*) *Seed hairs*. These comprise cotton, the whole of the cotton tree, vegetable silk, etc. (*b*) *Bast* fibres, forming the cambium layer of dicotyledonous plants, *e.g.* flax, hemp, jute, ramie, Sunn hemp, etc. (*c*) The *vascular bundles* from leaves, stems, or roots of monocotyledonous plants, *e.g.* New Zealand hemp, Pite or Agave fibre, Tillandsia, pineapple fibre, Manila hemp, true aloe fibre, etc., etc. Vegetable fibres contain cellulose as their fundamental substance, in addition to which they are (or at least some of them) more or less lignified. The larger the proportion of woody matter they contain, the greater their brittleness. Finally, they also contain in their cells and interstices so-called encrusting materials (ethereal oils, resins, starch, colouring matter, etc.), and ash.

Cellulose.[1]

As this substance forms the main constituent of all vegetable fibres, a knowledge of its chemical behaviour is of great practical importance. The vegetable fibres, even when in a pure state, do not behave entirely alike towards chemical reagents. Thus, for example, cotton has a greater power of resistance to bleaching powder solution than flax. The name Cellulose must therefore be considered as a generic term applying to several bodies of very similar nature. Cellulose is a colourless, inodorous, and tasteless substance (sp. gr. 1·27 to 1·45), which is insoluble in ordinary solvents. It belongs to the carbohydrates, and its percentage composition is expressed by the formula $C_6H_{10}O_5$, though its true formula is certainly a multiple of this.

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[1] A monograph on Cellulose has been published by Cross, Bevan and Beadle.

Starch is the most closely allied carbohydrate, and may also be regarded as the parent substance of cellulose. Nevertheless, the formerly assumed close connection between starch and cellulose has again become doubtful, since Skraup and Koenig[1] found that, unlike starch, it furnishes on hydrolysis not maltose, but another biose (cellobiose). Little is definitely known with regard to its actual constitution; it is spoken of as a triatomic alcohol, since when heated with acetic anhydride it furnishes a triacetyl derivative which, with potash, soda, lead oxide, etc., forms loose saline compounds which behave like alcoholates.

Pure cellulose is almost indestructible and can only be brought into a state of putrefaction in the presence of nitrogenous bodies. When heated it begins to turn brown at about 150° C.; when subjected to dry distillation it decomposes into water, CO_2, methane, ethane, methyl alcohol, acetic acid, pyrocatechin, etc. Furthermore, cellulose is a hygroscopic substance which cannot easily be brought to constant weight by drying. In water it is insoluble and is unchanged even by boiling for several hours; however, at 200° C. it dissolves in water, being itself completely decomposed.

Of greater practical importance is its behaviour towards acids and alkalis.[2]

Both these classes of reagent produce a change which is regarded as a hydration process, it being assumed that hydrocellulose ($nC_6H_{10}O_5 + nH_2O$) is formed. Whether a new chemical compound is actually formed, or whether—as assumed by Dreaper—the modified properties of the product (for instance, its increased affinity for dye-stuffs) is attributable to an increased absorption of water, is outside our province at present. In practice, at all events, the behaviour of cellulose towards alkalis is very different from what it is in the case of acids, its power of resistance being in the former case very high, especially when air is excluded. Used in the cold, strong alkalis effect a change, which is termed mercerisation, and will be dealt with later. Dilute acids produce no appreciable effect on cellulose, though it is destroyed by strong acids. This is the cause of the rotting of acidified fabrics made of vegetable fibres, and forms the basis of the process of carbonising wool (*q.v.*), in which the vegetable admixtures in the material are transformed, by the action of acids at a high temperature, into a very friable condition and can then be readily eliminated from the wool by mechanical means.

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[1] "Monatsheft f. Chemie," 1901, 1011.

[2] The manner in which various reagents act upon cellulose has been described by Grandmougin in "Zeitschrift f. Farbenindustrie," 1907, 2.

Cellulose dissolves, with decomposition, in a mixture of 1 part of sulphuric acid and about 3 of water, even at ordinary temperature. If cellulose, in the form of paper, be subjected to a short treatment with very strong sulphuric acid, the cell walls of the paper fibres undergo a superficial fusion, whereby the paper acquires the same external appearance as animal parchment. This paper is therefore known as vegetable parchment, and can be used for the same purposes as true parchment.

Whereas cellulose is left unstained by iodine, this reagent turns vegetable parchment blue, like hydrocellulose in general.

Organic acids, like oxalic acid, tartaric acid, citric acid, act upon cellulose in the same way as mineral acids, when the cellulose, *e.g.* cotton, is impregnated with the dissolved acid and exposed to a high temperature acetic acid, being volatilised by heat, has no action. The knowledge of this behaviour of cellulose is important, more particularly in the calico-printing industry.

Zinc chloride acts on cellulose like a mineral acid. The behaviour of cellulose towards nitric acid is important. When boiled with nitric acid of about 60 per cent. strength, cellulose is converted into oxycellulose. This oxidation product has a much greater affinity than cellulose for basic dye-stuffs, and is also of technical importance inasmuch as it is also formed by the action of other oxidising agents on cellulose—for instance, when bleaching powder is carelessly used in bleaching cotton.

When concentrated nitric acid is allowed to act on cellulose, especially in presence of concentrated sulphuric acid, nitrogenous bodies are formed which are regarded as nitrates of hydro-cellulose. This reaction, which is nowadays of high technical importance, was discovered by Schonbein in 1847. An original conception of the nature of these substances was advanced some few years ago by Zacharias[1] who regards the nitrocelluloses as adsorption compounds because, during the nitration of cellulose, a continuous series of bodies is formed, the whole behaviour of which exhibits nothing but changes.

If the formula $(C_6H_{10}O_5)_4$ be taken as the basis, the products are tetra-nitro- to dodecanitro-celluloses.[2] Strangely enough, the highest stage of nitration is attained by using a nitrating mixture containing water.[3]

Such of these compounds as approximate to octonitro-cellulose dissolve, in a mixture of alcohol and ether, to a viscous liquid, which has long been employed in medicine as "collodion," and which also plays an important part, nowadays, in the textile industry, in the manufacture of artificial silk. Other celluloses, however, of both higher and lower stages of nitration, are soluble in ether-alcohol, but they require to be suitably cooled, the process of solution being preceded by swelling up and disengagement of heat.

All the nitrocelluloses are explosive, and their discoverer, Schonbein, proposed to employ the more highly nitrated products (to which he gave the name of gun-cotton) as a substitute for gunpowder. These substances—which decompose explosively when heated, water, nitrogen, carbon monoxide, and carbon dioxide being formed—are, however, too disruptive for this purpose, but of late years they have found extensive employment in the production of smokeless powders and explosives.[4]

A material known as *celluloid* is prepared from the lower nitro products by dissolving them in molten camphor and pressing the mass while warm. This substance has a horny appearance, and is characterised by hardness, elasticity, transparency, and principally by the fact that when merely dipped in boiling water it acquires sufficient elasticity to enable it to be moulded into any shape under moderate pressure. In consequence of these valuable properties, celluloid is now largely used in the production of a large number of imitation articles, *e.g.* ivory, tortoiseshell, coral, collars, etc.

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[1] "Zeitschrift f. Farbenindustrie," II, 233.

[2] Ost, "Zeitschrift angewandte Chemie," 1906, 993; Green, "Zeitschrift Farbenindustrie," 1904, 309.

[3] Lunge und Bebie, "Zeitschrift angewandte Chemie," 1901, 483 and *seq.*

[4] Jute and starch have also been nitrated for the same purpose.

A number of regrettable accidents have occurred in the working up of celluloid. Although this substance cannot be termed directly explosive, since it cannot be exploded by shock, the dust given off during the working operations will explode on contact with a flame, and this has been the origin of the accidents mentioned.

Nitrocelluloses are also used in the production of pegamoid, which is a very fine substitute for leather, and is made by repeatedly coating cotton fabric with an alcoholic solution of nitrocellulose mixed with oil and a mineral pigment.

The resistance of cellulose to alkalis, especially in the absence of air, has already been mentioned, and this circumstance has to be borne in mind in bleaching works where vegetable fibres are boiled with alkaline liquids. Treatment with strong alkali in the cold produces the effect known as mercerisation, and if such a cellulose be treated with carbon disulphide vapour, a mass (a xanthogenate) capable of numerous industrial applications is obtained. According to its consistency the product may be used as an adhesive, loading or finishing ingredient, and it may also be cast in moulds and dried, the resulting transparent horny mass being cut and polished. The name "viscose" was applied to this product by its discoverers, Cross, Bevan, and Beadle (1892).

Reference may also be made to Vignon and Cassella's endeavour to amidise the affinity of cellulose for basic dye-stuffs, by treatment with ammonia and calcium chloride at 100° C. It is, however, very doubtful whether any amidisation of the cellulose can really be effected in this way, and the process has not attained any technical importance.

Another point worth knowing is the behaviour of cellulose towards ammoniacal copper oxide (Schweizer's reagent), in which it dissolves, even in the cold, to a viscous solution, from which a cellulose partly changed into hydrocellulose can be precipitated, in the form of colourless flakes, by acids.

Among other reactions of cellulose may be mentioned that it is stained blue (through the formation of hydrocellulose) by strong sulphuric acid and iodine, and violet by zinc chloride and iodine. It gives no coloration with aniline sulphate, in contradistinction to lignin, which is turned yellow.

For the preparation of pure cellulose from crude vegetable fibres, and also for the quantitative determination of their cellulose content, use is made of the method of Hugo Muller, consisting in treating the material in question with bromine water and ammonia alternately. The crude fibre, after being boiled with water, is placed in a stoppered bottle with water, and is agitated with bromine water until the liquid acquires a permanent yellow tinge. The bottle is then closed, and is left to stand for several hours, the fibre being afterwards taken out, washed, boiled with dilute ammonia, and washed again. This combined treatment with bromine water and ammonia, when repeated 1-3 times, furnishes a snow-white and almost perfectly pure cellulose.

Artificial Silk.

Count Chardonnet was the first to succeed in producing from collodion threads suitable for use as textile fibres, although Tudemar, in 1855, and Swan, in 1883, filed patents for a process of this kind, whereas Chardonnet's patents were only taken out in 1885. The process was improved more particularly by Lehner.

Preparation. Cotton that has been purified by boiling in lye is nitrated in a mixture of nitric and sulphuric acids in an earthenware vessel. The resulting nitrocellulose is drained in a whizzer, washed until it contains only about 10 per cent. of acid, and transported in small trucks running on wooden rails to drying stoves—which should be at least 15 yds. away from the factory—where it is spread on racks and partially dried in an ammoniacal atmosphere at 30° C., great care being necessary on account of the risk of explosion.

Fortunately, complete drying is neither essential nor desirable, the moist nitrocellulose presenting the advantage that it sets as soon as it issues from the spinning apparatus, and produces a more solid thread during the after treatment, so that partial drying is regarded as sufficient. This semi-dried product is placed in an iron pan and sent back, on the same trucks, to the factory where it is converted, by means of a mixture of about 40 parts alcohol to 70 of ether, into a 15-20 per cent solution. The latter, after being purified by forcing it through a cotton filter by compressed air, is fed by the same means into the spinning apparatus, the chief feature of which is a number of horizontal tubes provided with lateral capillary nozzles through which the collodion is forced, in the form of slender filaments, into water, where it is immediately solidified. These threads are seized by tongs and passed in groups through a collector to a reel above the apparatus. The threads are put through further treatment similar to that of real silk, being dried, sorted, bleached, rinsed, twisted, and reeled into hanks of definite length. The next stage is to remove the danger of the threads exploding, since otherwise they could not be used as textile yarns, and for this purpose they are denitrated, a highly important and delicate operation. In this connection also, Chardonnet was the first to point out the right method by using sulphides, and the technical importance of artificial silk dates from this discovery (1890). The best denitrating agent is sodium hydrosulphide, the ammonia salt being too dear and the lime salt making the fibre too hard. Favourable results have also been obtained with Richter's patented process, in which cupric chloride is used. When the collodion threads are treated for some time in a lukewarm solution of this kind they lose about three-fourths of their nitrogen, and consequently their explosive character. They are then washed in slightly acid water, and dried.

To carry on the manufacture of artificial silk in the most economical manner, the endeavour is made, on the one hand, to recover the alcohol-ether solvent as completely as possible, by condensing it in the water troughs underneath the spinning frames, and, on the other, to regenerate the spent acid from the nitration process.

The loss in weight (about 10 per cent.) sustained by the artificial silk in denitration can be made good by impregnating it with various substances, such as ammonium phosphate, this treatment also lowering its inflammability.

Latterly, attempts have been made to improve the spinning qualities of the collodion solution by lowering its viscosity.

The technical success attained by Chardonnet silk led to the introduction of a series of more or less similar processes, most of which, however—such as those of Vivier, Lehner, Cadaret, Millar, Langhans, etc.—made only temporary headway, if at all.

According to Vivier, a mixture of trinitro-cellulose, fish glue, and gutta-percha is dissolved in glacial acetic acid; the composition of the solidifying liquid is kept secret. The finished product has a brilliant lustre, and is said to cost only about 1s. 6d. per cwt. Lehner dissolves purified silk waste in concentrated acetic acid, and mixes therewith a solution of nitrocellulose in wood spirit and ether; turpentine and chloroform are used as the coagulating liquid.

Cadaret nitrates purified cellulose, bleaches it with aluminium hypochlorite, and dissolves it in acetone, ether, alcohol, toluol, glacial acetic acid, and castor oil, the resulting mass being broken down and worked by hot cylinders to make it plastic, and treated at the same time with a solution of gelatine, albumen, or other proteid substance, in glacial acetic acid. The plastic silk-like mass is pressed into the spinning apparatus, and is finally treated with tannin to impart elasticity. The cost price is said to be about 2s. 6d. per cwt.

Langhans does not use nitrocellulose at all, but claims rather that cellulose can be so modified by repeated treatment with sulphuric acid of varying strength that it can be used for the production of silk-like threads.

Adam Millar makes artificial silk from gelatine solutions, the filaments being rendered insoluble by treatment with bichromate. According to a patent taken out by Bernstein, formaldehyde is used for this purpose. The product known as Vandura silk does not appear to have come on the market at all.

Special mention should be made of the following: (1) Pauly silk; (2) Viscose silk; (3) Acetate silk.

Pauly Silk (Cellulose silk, Elberfeld or Oberbruch artificial silk).—

Cellulose is soluble in both ammoniacal copper oxide and zinc chloride, and solutions of this kind—which are viscous like collodion—can be made into lustrous threads in the same way as described for Chardonnet silk. Zinc chloride, which was proposed by Dreaper and Tompkins, has not been found suitable, though the process, which gives a product similar to mohair, has not been abandoned—but, on the other hand, the employment of ammoniacal copper oxide has met with great technical success. The process, which was first proposed by Despeissis, was patented in 1897 by Fremery, Urban and Bronnert. The threads are solidified in dilute sulphuric acid.

The drawback of the process is that it will not furnish such fine counts as the Chardonnet process, but it is also clear that a method in which the transformation of cellulose into the dangerous nitro compound is entirely dispensed with, and there is no need to use expensive solvents (ether-alcohol), presents great advantages over the Chardonnet process. The difficulty to be overcome resides in the low solubility of cellulose in ammoniacal copper oxide. This, however, can be increased in various ways, such as by working at the lowest practicable temperature, or by forming the ammoniacal copper oxide at the same time that the cellulose is dissolved, the cellulose and copper turnings being suffused with ammonia and exposed to the air. Another way is by temporarily mercerising the cellulose. Moreover, it is stated that cellulose dissolves better in an ammoniacal solution of copper carbonate than in the ordinary solvent. The best method of producing a cellulose silk would appear to be by converting cellulose into hydrocellulose, by treating it with commercial sulphuric acid, and dissolving the product in caustic soda.

Viscose Silk. This product is manufactured according to the Stearn process (Ger. Pat. 108511 98) by forcing solutions of viscose through capillary orifices, and solidifying the resulting threads in sal ammoniac solution. The product requires steaming in order to decompose the xanthogenate completely. Viscose silks are the cheapest of all artificial silks.

Acetate Silks.—Many attempts have been made, and especially in the works of Count Henckel-Donnersmarck at Sydowsau, near Stettin (where the Stearn artificial silk process was elaborated, from 1901 onward), to obtain a suitable material for artificial silk manufacture by acetylising cellulose. These acetate silks are claimed to be of excellent quality. Unlike Chardonnet silk, they do not swell on contact with water, and are therefore stronger and able to resist the action of water completely. They are also claimed to be the best insulating material for electrical conductors.

As regards properties, the artificial silks have a beautiful gloss, nitrocellulose silks being more highly lustrous than real silk. On the other hand, the tensile strength is low, that of nitrocellulose silk being only about half that of real silk. Their ductility being also low, they cannot be used as warp in weaving fabrics, since they could not stand the tension in the loom. Furthermore, in the wet condition particularly, artificial silk is very friable. Pauly silk, though stronger than Chardonnet silk, is still too weak to be woven into garments, and it follows, therefore, that the sphere of application of the artificial silks is limited, though their uses are manifold, including trimmings (low counts also for lace-making), curtains, upholstery and cravat fabrics, for decorative threads in woollens, etc. Thick threads or ribbon, made by uniting several artificial silk filaments together, are used to replace horsehair in making healds, as trimming for ladies' hats, for wigs, and as artificial plaiting straw. For these purposes the stiffness of artificial silk makes it very suitable, and it has the additional advantage of being more easy to clean from dust than real silk.

Behaviour in Dyeing.—Chardonnet silk should be dyed in a lukewarm bath (not over 50° C.), and it is not advisable to exceed 50° C. with Pauly silk. The former silk has a high affinity for basic dye-stuffs, and can be dyed direct with these, though the dyeings will be richer and much faster if a previous treatment with tannin be given, as in the case of cotton. Conversely, Pauly silk has the greater affinity for saline dyes.

Artificial silks should be dyed by immersion for ½-1 hour in a large quantity of dye liquor, then well stretched and dried. In some cases, *e.g.* dye salts and sulphur dyes, an addition of Monopol soap (*q.v.*) is beneficial, as it softens the material.

Viscose silk behaves like Pauly silk in dyeing; but the acetate silks will not dye well unless alcohol or acetone be added to the bath.

Commercial artificial silks are two to three times heavier, length for length, than real silk. The only loading practised is in black dyeing, the weight being increased about 40-50 per cent., and the tensile strength also improved.

The nitrocellulose silks give the diphenylamine reaction and are stained blue by iodine, but Pauly silk and the cellulose silks do not give these reactions. In respect of behaviour towards strong reagents, such as acids, zinc chloride, alkalis, etc., the artificial silks are very much alike, though in all cases Pauly silk has a greater resistance than the nitrocellulose silks. Under the microscope the artificial silks exhibit the following differences. Chardonnet silk is of irregular cross section, and therefore the fibres show longitudinal striations like Tussah silk, etc., which is not the case with Pauly silk. According to Silvern, the cross section of viscose silk is characteristically sharp edged.

The artificial silks differ from real silk by their greater thickness, double refraction and insolubility in strong alkalis, ammoniacal nickel oxide, and alkaline copper glycerate; also, under the microscope, by the fact that, unlike true silk, they swell when moistened with water, so as to increase ¼-⅓ in width. The acetate silks, however, as already mentioned, do not exhibit this last-named property.

The hygroscopicity of artificial silks is 1-2 per cent. greater than that of real silk.

In 1908 the annual production of artificial silks amounted to over 3000 tons, in 26 works, of which 8 were in Germany, 6 in France, 4 in Switzerland, 3 in Italy, 2 in England, and 3 in Austria-Hungary.

(1) SEED HAIRS: COTTON, TREE WOOL, VEGETABLE SILK.

Cotton.

Origin and Definition.—The name Cotton indicates the downy substance found in the seed capsules of plants of the species *Gossypium* (family *Malvaceæ*). It grows out of the seed, and is therefore a seed hair consisting of a single cell. The seed is covered with a very coarse, generally yellow, brown, or dirty green underwool, whereas the valuable cotton hairs are much longer and for the most part colourless.

For the purpose of cultivation only about five species of *Gossypium* are important, although about twenty are known. They are shrub or tree-like plants measuring [illegible] to 24 feet in height, and thriving in all warm countries, their principal habitat being North America and India.

Gathering.—As soon as the cotton fruit is fully ripe, which occurs in August, September, and October, the capsules burst open and the cotton exudes. This is the most favourable moment for the harvest, and the capsules are plucked from the plant, the seeds and cotton being then taken out of the capsules. The cotton is separated from the seeds by means of so-called ginning machines, of which there are two chief systems in use: the roller gin and the saw gin. The former consists of rollers which seize and draw in the cotton fibre, whereas the seeds cannot pass through but are driven back. The saw gin consists of saw plates, which are mounted on rollers, the teeth projecting through a narrow grid through which they draw the cotton fibres, leaving the seeds to fall to the ground on the other side.

The seeds are used for the manufacture of cotton-seed oil, whilst the cotton is pressed and sent to market in bales.

Historical. Cotton has been known and used in Peru and India from the earliest times, and also seems to have been cultivated at a very early period in Persia. Thence it probably found its way to Egypt, where it has been known ever since about the fifth century B.C. At about the same time the Greeks and Romans, who previously had known only wool, began to wear cotton clothes.

The European cotton industry only began to come into importance at about the end of the eighteenth century, and may be considered to date from the year 1772, when the first cotton fabric was produced in England. At that time the supply of cotton was chiefly obtained from the Levant and Macedonia, but, later, America became the chief exporter; and since the North

American War, India and Brazil have also successfully competed in the cotton trade. At the present time the demand for cotton is principally covered by North America, India, Egypt, and Brazil. The trade is now mainly centred in England, particularly in Liverpool, and the English cotton trade is the largest in Europe. The yearly consumption of cotton in the whole of Europe is estimated at about one million tons.

Commercial Varieties. In commerce two principal varieties of cotton are known, namely, "long staple," the fibres of which are 1 to 2 inches long, and "short staple," from ½ to 1 inch. The whiter, cleaner, and more silky the cotton the higher the value, but that consisting of short nepped fibres is inferior. The best and most highly prized of all is Sea Island cotton from *Gossypium Barbadense*, the finest grade of this being also known as "long Georgia," which at present is mainly grown in Florida.

Structure. The cotton fibre is a single, elongated, conical, epidermal cell, the upper extremity of which is closed, whilst the lower end, which was attached to the seed, is broken off irregularly. Under the microscope the fibre (see Fig. 1) appears as a granular striped band, mostly twisted in the shape of a corkscrew. This is more particularly evident when the fibre has been moistened with water. This highly characteristic feature may nevertheless be absent in places.

The fibres are not cylindrical but flat, though this is sometimes not the case (in parts) in the finer kinds. There is a central cavity known as the *lumen*, which is generally small in proportion to the cell walls. Consequently the latter are often very thick, though in common grades the lumen is three or four times as broad as the cell wall. Occasionally the lumen is absent altogether, and the fibre is then known as dead cotton, being the immature and imperfectly developed hairs; these then take the dye with far greater difficulty than the normal fibres. Viewed under the microscope it appears perfectly transparent, only the edges being visible.

Externally the cotton fibre is surrounded by a fine skin—the cuticle. The substance from which this is formed does not behave exactly like cellulose, and is considered as a conversion product of the latter under the influence of light and air.

Whereas cellulose is rightly soluble in ammoniacal copper oxide and concentrated sulphuric acid, the cuticle takes a long time to dissolve in this reagent. On treating the fibre with the first reagent under the microscope, the phenomenon so highly characteristic of cotton is observed; the internal substance, consisting of cotton, turns gummy, swelling up and bursting the cuticle in isolated places. The cuticle appears as though binding the cellulose as with a cord, whilst in other places it hangs in loops. Finally, the cellulose is completely dissolved, and the fragments of torn cuticle float in the solution (Fig. 2).

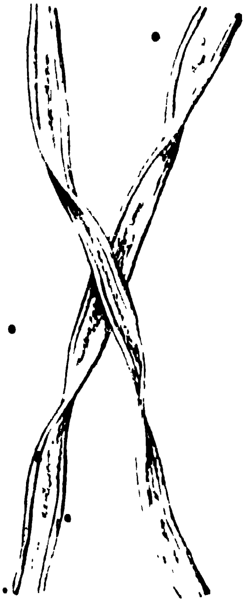
Fig. 1.

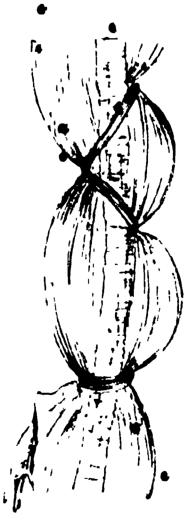
Fig. 2.

As the bast fibres, which will be described later, are devoid of cuticle, they do not exhibit this characteristic behaviour when treated with ammoniacal copper oxide. Consequently this reaction affords a valuable means of differentiation. It must, however, be mentioned that cuticle is not invariably present on all cotton, especially after strong bleaching, since under these circumstances the cuticle is mostly destroyed.

Chemical Composition.—Raw cotton consists of (in round figures) 87 to 91 per cent. cellulose, 7 to 8 per cent. water (cleaned cotton mostly a little over 5 per cent.), 0·4 to 0·5 per cent. wax and fat, 0·5 to 0·7 per cent. of protoplasmal residue, and 0·12 per cent. ash, together with a very small quantity of colouring matter. The sp. gr. of air-dried cotton is 1·5.

Behaviour of Cotton towards Reagents. In the main, cotton behaves similarly to cellulose, except that towards water it is less absorbent, probably due to the greater fineness of division of precipitated cellulose. It is however desirable that the changes sustained by cotton under the action of various reagents should be accurately investigated. The increased affinity of treated cotton for basic dye-stuffs and mordants is of value only in so far as it confirms the fact that some change has taken place. For example, if a specimen of cotton has been partially transformed into oxycellulose by careless treatment with bleaching powder, this can be detected by dyeing it with methylene blue, the attacked portions coming out darker in colour. A similar result is obtained by steeping the specimen for some time in a weak solution of alum and then dyeing with alizarin. The same effect, however, is produced if the cotton has been corroded by an acid or exposed to high temperature (about 150° C.) for some time.

According to M. Philip particles of oxycellulose in cotton may be detected by boiling the material with 10 per cent. Fehling solution for a quarter of an hour on the water-bath. After rinsing with water, the oxycellulose will show up red. Unfortunately, this reaction, too, is not characteristic, appearing also when cotton has been affected by dry heat, long storage in a wet condition, or by treatment with acids. In fact, even some kinds of raw cotton, that have not been through any treatment at all, will give the same reaction.

There is only one reaction that will enable a differentiation to be made between cotton which has suffered conversion into oxycellulose and such as has been changed by heating or acids, namely, that transformation into oxycellulose lowers the affinity of cotton for dye salts, whereas the other agents have an opposite effect.

Mercerising Cotton.[1]

In 1844, John Mercer found that cotton underwent a remarkable change when treated in the cold with strong alkalis, sulphuric acid, or zinc chloride, the fibres contracting longitudinally, becoming more compact and acquiring an increased affinity for dye-stuffs.

The shortening of the fibres constituted a great drawback to the process and prevented its technical utilisation until a comparatively recent date, its chief use in the earlier days being for the production of crepon effects in calico printing. Remarkably enough, neither the inventor nor other textile experts hit upon the evident idea of obviating the drawback by stretching the cotton during the mercerising process, and it was not until half a century later (1895) that a patent was taken out by Thomas and Prévost for a process which exercised an enormous influence on the entire cotton industry, through the discovery that when cotton is mercerised under sufficient tension to prevent the contraction of the fibres, the goods acquire a more or less considerable glossiness.[2] Attempts have been made to belittle the merits of Thomas and Prévost by reference to an older patent for the same process by Lowe, but it is quite certain that they were the first (in their second patent) to recognise the production of lustre on cotton mercerised under tension as a new technical effect.

The endeavours made to prevent the contraction of the cotton by additions to the mercerising liquor, met with no technical success, for even though an addition of glycerine, alcohol, and other agents is more or less effective in this respect, the lustre of the fibre is far inferior to that obtained by mercerising with alkali alone, in conjunction with stretching. For the same reason (and also partly on account of the expense) other agents that have been proposed, such as sodium sulphide, iodides, etc., have proved technically worthless. Nitric acid alone—and even then only in combination with tension—gives anything like the same gloss as alkali.

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[1] A monograph on this subject has been published by Gardner.

[2] An explanation of this was presented by J. Hubner to the International Congress of Applied Chemistry, Berlin, 1903.

Temperature plays an important part in the mercerising process. Hot liquor will not produce the effect at all, whereas the influence of low temperatures is such that at 0° C. a liquor of 20° B. strength will give the same result as one of 30° strength at ordinary temperature.

In carrying out the process in practice, the mercerising vats are fitted with cooling devices, which cool the liquor (of about 25° B. strength) down to 10-15° C. This cooling is necessary to counteract the heat generated in the process itself, and also (in the case of raw cotton especially) that produced by the chemical action of the liquor on the impurities in the material.

A third factor which operates during the process is the quality of the cotton itself. It has been found that Egyptian (Mako) cotton and the long staple Sea Island cottons furnish the glossiest product, especially if the fibres have been laid parallel by combing. The explanation of this is that, when the cotton is placed under tension, only the longer fibres are stretched, the others merely suffering relative displacement. For this reason better results are obtained by mercerising twists, in which the individual fibres are more firmly embedded, than with single yarns. Hard-twisted yarns present a certain difficulty, inasmuch as the liquor does not penetrate right through them so easily; but this is overcome by boiling them (preferably with an addition of turkey-red oil or textile soap) and then mercerising them without any intermediate drying.

The material to be treated must be well gassed beforehand, in order to obtain a smooth surface, and of course it must not be put through any operation which would tend to roughen it.

Bleaching is not an advisable preliminary to mercerisation, as it reduces the lustre, hardens the feel of the material, and the loss in weight on mercerisation is then sometimes very considerable. The best plan is to boil the material first, then mercerise, and finally bleach.

After mercerising, the cotton is squeezed, washed, and soured.

Fabrics of mixed wool and cotton must be mercerised at a low temperature (0° C.), owing to the low resistance of wool to alkalis, and must at once be immersed in a bath of fairly strong sulphuric acid, to neutralise the alkali as quickly as possible.

If the goods were to be rinsed with water, a weak liquor would result, which—as will be seen later—attacks wool more powerfully than stronger lyes.

A great deal of work has been done, and much has been written, with regard to the manner of carrying out the mercerising process. Speaking generally, there are two distinct types: (1) Tension during the mercerising process (used more particularly for yarns), and (2) Tension after mercerising (applied to fabrics). The second requires a considerable amount of power. The machines employed differ, according as the goods under treatment are in the form of yarn or fabric.

Mercerising Yarn.—The machines used, *e.g.* those of Hauboldt, Cohnen, Hahn, Kruse & Linder, are mostly automatic, the hanks being placed over two rollers, which can be moved closer together for that purpose and then drawn apart for the purpose of producing tension. The stretching is gradual at first, being finally increased to the limit the fibres will stand without rupture, because the higher the tension the brighter the lustre. It is true that highly stretched cotton does not give such full shades when dyed as that which has been mercerised under lower tension, but this drawback is more than counterbalanced by the advantages obtained.

Before the maximum tension is applied, it is advisable to damp the cotton with water, which softens it and enables it to stretch better. It is also a good plan to work the yarn round in the bath.

The treatment does not take long, the maximum effect of the liquor on the cotton being attained in a few minutes. Next comes squeezing between rubber rollers (mostly effected automatically by the machine), followed by rinsing with a suitably arranged spraying pipe.

Quite a different method of applying the tension is that employed by the firm Kleinwerfers Söhne, who make use of a centrifugal whizzer mounted on a horizontal axis. The yarn is laid on a perforated drum and is subjected by the centrifugal force, to a constant tension which prevents contraction. The mercerising liquor, which is admitted axially into the drum, is distributed uniformly through the yarn by the same force.

Rinsing and drying are also done in the machine, which presents the great advantage that breakage of the yarn is impossible.

Mercerising Piece Goods. The chief machines for this work are those of David, Hauboldt, Jeanmaire, Simon, and others. The usual practice is to soak the goods in lye first, and stretch them afterwards, a certain tension, however, being put on the material during its passage through the liquor—generally full width, in a padding machine. The goods are next stretched in a stenter (which takes only about ¼ to ½ a minute) and washed. The stretching may also be effected by rolling pressure, in a machine such as the Bernhardt, in which the goods, mounted on a roller, are immersed in the mercerising bath, the cloth unrolling on to a second roller lying on the first one. These two methods of stretching differ mainly in the fact that the stenting machine acts principally on the weft threads, whereas the Bernhardt method stretches the warp threads.

The chief advantages of mercerising reside in the increased affinity the cotton acquires for dye-stuffs, and in that the quality of the goods and of the dyeings is improved, so that a large proportion of the cotton goods of the present day are mercerised, even though the production of a glossy surface is not desired.

Lange's test for distinguishing between mercerised and unmercerised cotton is to treat the sample for a few minutes, in the cold, with the solution of zinc chloride and iodine usually employed in testing the fibre. The resulting blue stain easily washes out in the case of unmercerised cotton, but is more difficult to remove in this way in the case of mercerised goods. If dyed fabrics are to be tested, they must first be decolorised.

Cotton is a very resistant material, but if allowed to remain in a damp condition—especially when it contains dressing—it is liable to attack by mould fungi, which produce yellow to dark brown stains. In the early stages of attack, these stains can easily be got rid of by energetic washing, but later on this is no longer feasible, and by that time the fabric or yarn will have become more or less corroded. The best method of prevention is to store the goods in dry, well-ventilated warehouses.

The more or less violet stains found on cotton goods are of a different character, being due to the iron tannate produced by the action of ferruginous water, etc., on the tannin present in the seeds left in imperfectly-cleaned cotton.

Finally, it may be mentioned that the frequently observed spontaneous ignition of cotton is caused by the respiratory action of bacteria.

Bombax Cotton from the Cotton Tree.

A kind of cotton similar to that of the cotton plant has, from time immemorial, been collected from the fruit capsules of plants of the Bombax family (allied to the *Malvaceæ*) in the countries of production, and utilised in various ways.

The Bombaceæ thrive in all tropical countries, but are little known in Europe. The cotton is found in commerce under various names, such as vegetable down, ouate végétale, Edredon vegetal, Pattes de lierre. Bombax cotton is soft, lustrous, and white to yellow-brown in colour. Being seed hairs, the fibres are morphologically similar to true cotton, from which, however, they differ in the absence of the spiral twist, the presence of reticulated thickenings of the cell wall, and in the inferior thickness of the latter; consequently, they are much weaker than true cotton and cannot compete with it. The fibre is chiefly used for wadding and as an upholstering material, though occasionally it is mixed with cotton and spun. Bombax cotton may be distinguished from true cotton by the pale yellow tinge imparted by iodine and sulphuric acid or aniline sulphate, which indicates a slight degree of lignification.

Vegetable Silk or Asclepias Cotton.

The seeds of a number of *Apocyneæ* and *Asclepiadeæ* (mostly tropical) are provided with a tuft of long fibres possessing a beautiful silky lustre and known as vegetable silk. On account of their beautiful appearance many attempts have been made to spin these fibres, but failed by reason of their brittle character and low tensile strength.

The fibre is readily distinguished from cotton by its lignification, and from Bombax cotton by characteristic thickened strips, revealed in the cell wall under the microscope.

(2) Bast Fibres: Flax, Jute, Hemp, and Ramie.

Flax.

Definition and Origin. Flax consists of the bast fibres from plants of the Linum family. The species *Linum usitatissimum* being specially suitable for its production.

The true home of the flax plant is unknown, but it yields, especially in northern countries, a good bast suitable for the preparation of flax. This is the reason why nearly all flax-growing countries get their seeds from the Russian Baltic provinces.

Preparation. In order to obtain a good fibre the plants must be gathered before they are ripe, the proper time being indicated by the change in the colour of the seed capsules from green to brown. The harvest is carried on from June to September, the whole plants being pulled out of the ground, dried on the field, and finally rippled with iron combs to separate the stalks from the leaves, lateral shoots, and seed capsules. The bast fibres amount to about 70 to 75 per cent. of the stalks. These latter are now subjected to a process of retting, a kind of fermentation, the object of which is to decompose and render soluble the glutinous and intercellular substances, which cause the bast fibres to stick together and to the woody matter of the stalk.

This operation is the most important in the entire preparation of flax, influencing, as it does, the final product in the highest degree. It is performed in various ways: water retting, dew retting, mixed retting, warm-water retting, steam retting, and chemical retting. In *water retting* the flax stalks, tied in bundles, are placed in baskets and left for ten to twenty days in running or stagnant water. At first a turbulent acid fermentation is set up, and is followed by a quiescent alkaline fermentation. The stalks are taken out from time to time in order to see whether they are sufficiently retted, which may be recognised by their feeling soft and by the woody parts separating easily from the fibres. When this is accomplished the retting must be stopped immediately, since, if allowed to continue, the fibres would be damaged by over-retting. In *dew retting* the flax stalks are spread out in thin layers on a meadow, and moistened from time to time. This takes much longer than water retting. In *mixed retting* the first part of the fermentation is carried on in water, and the second completed on the grass.

These three methods are also known as "*natural retting*," and the water-method being the cheapest is therefore the most in favour, notwithstanding that it does not yield a very handsome product, especially when performed in hard or ferruginous water. Over-retting is also very liable to occur, and an additional drawback arises from the intense putrescent smell given off, in consequence of which water retting must always be carried on at a distance from human habitations.

Natural retting being also greatly dependent on the weather, attempts have been made to supersede it by artificial processes, chief among which is the *warm-water retting* method invented by Schenk. It is similar to ordinary water retting, but is carried on in tanks wherein the water is warmed up by steam to about 35° C. The operation takes from two to three days, and furnishes a product superior both in quality and quantity to that obtained by natural retting; and is, moreover, the most rational method of procedure. Occasionally the bundles are subjected to an alternating treatment of steam and hot water, the process being then termed *steam or hot-water retting*.

Among the chemical methods of retting that have been proposed, that of Baur has been found satisfactory. It consists in first treating the flax stalks for an hour, below 100° C., with dilute sulphuric acid, and then washing out with a weak solution of carbonate of soda, the pectic acids precipitated (in the form of jelly) on the fibres by the first treatment. The fibres obtained by this interesting process are much finer than those prepared in any other way.

The flax stalks, having been retted by one or other of the foregoing methods, are well rinsed and dried; it is, however, highly advisable to first pass them through rollers, by which means the greater part of the mucinous matters enveloping the fibres are expressed, and the subsequent separation of the fibres from the wooden matter is greatly facilitated. To effect this separation, the dried stalks are subjected to the following mechanical operations:—

1. *Crushing or beating*, which consists in breaking down the woody matter by the aid of mallets or a stamping mill.

2. *Breaking.* The stalks are passed between the fluted rollers of a flax breaking machine, whereby the woody matter is still further broken down, the greater part being at the same time removed.

3. *Scutching.* The object of this treatment is the complete removal of the woody matter, and it is effected by beating the vertically suspended flax with blunt wooden knives. The work is done either by hand or in a machine, the fibre suffering less damage in the former case than in the latter.

4. *Hackling.*—The scutched flax stalks are drawn through a series of successively finer steel combs, which separate any fibres that still remain stuck together, and draw them out parallel. This work is also done by hand or machine.

Historical. Flax is the oldest of all textile fibres, and has been cultivated in China from time immemorial. Linen wraps, some characterised by extreme fineness, have been discovered in lake-dwellers' habitations, and the wraps enveloping Egyptian mummies also consist of flax fibre.

Commercial Varieties and Statistics. Flax is put on the market in the form of long, soft, lustrous fibres, the colour of the best kinds being a pale blonde. If the flax has been covered with mud whilst retting it will have a greyish colour, and is particularly soft. Over-retted flax is dull and brittle.

The number of chemical varieties of flax is very large. The best kinds are produced in Ireland and Belgium, though a few French and Dutch varieties may also be included in the first class. The beautiful lustrous Italian flax is also highly prized, but Russian, Prussian, Silesian, and Austrian flax, although long in fibre and strong, are of inferior fineness. Egyptian flax is characterised by its extreme length, which averages about forty inches, whereas Silesian flax, for instance, averages only eleven inches in length. The annual consumption of flax in Europe is estimated at about 300 000 tons. These figures, however, cannot lay claim to any degree of accuracy, since the preparation of flax still remains to a large extent a home industry, and as such escapes the attention of the statistician.

Structure.—Under the microscope the flax fibre appears as a long, straight, transparent cylindrical tube of uniform thickness, either smooth or longitudinally striated, and frequently exhibiting transverse cracks. In many places it presents nodes and displacements, which cause it to look as though articulated. These nodes, which are specially characteristic of flax fibres, are rendered darker by treatment with zinc iodo-chloride, and then become very clearly visible.

The natural ends of the fibres are sharp pointed and mostly attenuated, the cell walls are very thick, and the lumen is so narrow that it appears under the microscope as merely a black streak. The cross section of the fibre is also very characteristic, exhibiting a number of polygonal cells, in the centre of which the lumen appears as a yellow dot (in consequence of its yellow protoplasm). This is seen very clearly when the fibre is treated with zinc iodo-chloride, the traces of protein in the lumen being stained yellowish-brown, and the cell walls red-violet. Sometimes, however, and especially in fibres taken from the lower part of the stalk (hypocotyl fibres), the cells exhibit a

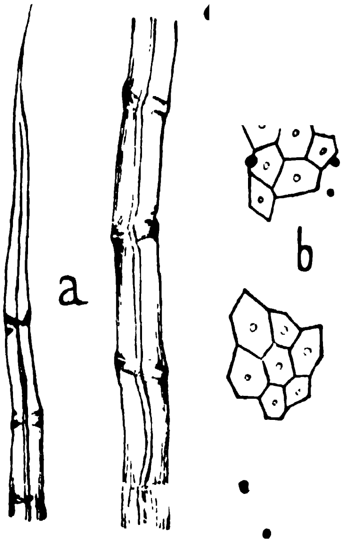

FIG. 3.—Flax fibres: *a*, Longitudinal view; *b*, Cross section.

rounded shape similar to those of hemp. Occasionally, also, the ends are forked, and in some cases e.g. flax from the Russian steppes the lumen is broad, and interrupted in places, so that the fibres appear to be divided into compartments. Some of them assume the form of flat bands, looking almost like cotton, with occasional constrictions to an apparently solid mass.

Composition. The purified flax fibre consists of almost pure and quite unlignified cellulose, so that, like cotton, it is stained blue by iodine and sulphuric acid, and is not tinged yellow by aniline sulphate.

In the air-dry condition flax contains about 5½ to over 7 per cent. of water, and various amounts of cellulose, pectin substances, fat, wax, and ash, differing according to the preparation.

According to Vignon the specific gravity of flax fibre is 1·5.

Behaviour Towards Reagents. In this respect flax behaves very like cotton, though, mainly owing to the structure, it takes up mordants and dyes less readily than the latter. Moreover, the impurities of crude flax especially the brown pectin substances are more difficult to remove than in the case of cotton, and consequently the operation of bleaching flax is harder than with cotton. Flax fibre is more susceptible than cotton to the action of bleaching powder. When treated with ammoniacal copper oxide, it swells up considerably, without, however, quite passing into solution.

Hemp.

Definition and Occurrence. Hemp consists of the bast cells of the hemp plant *Cannabis sativa*, which, like the flax plant, thrives in moderate subtropical climates. In hot countries, India, for example, it yields a defective fibre, though, on the other hand, it produces large quantities of seeds, which are strongly narcotic and therefore used in the preparation of delicacies like *hasheesh*.

Preparation. This is effected in the same manner as flax, though occasionally the bast is stripped off from the plant whilst still fresh, the product in this case being valued on account of its length and purity.

Historical.—Like flax, hemp belongs to the oldest of the textile fibres. Of all European countries it seems to have been longest cultivated in the south of France.

Commercial Varieties and Statistics.—In commerce a distinction is drawn between clean and stripped hemp. The small waste fibres obtained in hackling are called tow. Since hemp is for the most part coarse and of dark colour, and is very difficult to bleach, none but the very finest qualities are spun; the great bulk of the article being used in the manufacture of string, cord, rope, hawsers, etc., for which its great strength renders it particularly suitable.

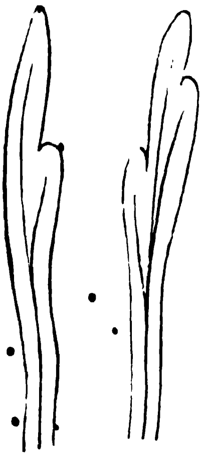

Fig. 4. Ends of flax fibre.

The handsomest varieties of hemp come from Italy, and among these Bologna hemp occupies the first place, being fairly white, lustrous, very fine, and flexible. Next to the Italian kind comes Grenoble hemp. The largest quantities are, however, obtained from Russia, whilst other hemp-producing countries include North America, Alsace, the south of Baden, Prussia, and Austria. Mention should also be made of the African giant hemp, which, as its name implies, is characterised by great length, the fibres measuring upwards of ten feet long.

About 500,000 tons a year are produced in the whole of Europe, one-fifth of which quantity is grown in Russia.

Structure. Examined under the microscope the fibre of hemp is very similar to flax, exhibiting displacements, longitudinal fissures, and transverse cracks. On the other hand, the lumen is broad and only contracts to a narrow line near the tip; moreover, the entire fibre is less regular in thickness than flax. The ends of the fibres are highly characteristic, being very thick walled and blunt (see Fig. 4), frequently branching sideways, and thus affording a ready means of distinguishing this fibre from flax when examined under the microscope by a low and high power in succession. (A similar appearance is observed in the hypocotyl fibres of flax.)

The cross section is also different from that of flax, the cells being mostly in dense groups, with rounded corners, and giving a yellow margin when treated with iodine and sulphuric acid. The lumen, instead of being circular, is elongated, frequently branched, and devoid of contents.

Composition. In addition to cellulose, hemp fibre contains a not inconsiderable quantity of woody matter, differing in this respect considerably from cotton and flax. According to Vignon, the specific gravity of hackled hemp is 1·48.

Behaviour Towards Reagents. Iodine and sulphuric acid stain hemp fibre green to dirty yellow, the various strata in the cell walls assuming different colours. Unlike the fibres previously described, hemp is stained slightly yellow by concentrated nitric acid. Treated with ammoniacal copper oxide the fibre turns blue to green, swells up in bubbles, without, however, dissolving, and exhibits delicate longitudinal striations. The same is, however, also sometimes noticeable in the case of flax.

Jute.

Definition and Occurrence.—Jute consists of the bast fibres of several varieties of *Corchorus*, indigenous to India. These plants yield such an enormous quantity of fibre that land planted with jute gives a crop from two to tenfold greater than is obtained from flax or hemp.

Preparation. The jute fibre is obtained from the plant by cold-water retting, and is cleaned by scutching and hackling. Great care, however, is necessary in carrying out the first-named operation owing to the ease with which jute becomes over-retted.

The fibre is prepared for spinning by steeping it in an emulsion of oil and soap previous to hackling.

Historical.—Jute has long been the most important fibre produced in India, and has grown in importance in European commerce since 1860, when the Crimean War led to a scarcity of Russian hemp.

Commerce, Statistics, and Uses.—Jute comes on the market as a yellow to French-grey fibre. The coarser kinds are worked up in the production of coarse fabrics, sacks, packing cloths, and the like, whilst the finer kinds, in which the undesirable property of growing darker with age is less apparent, are employed for making carpets, curtains, and heavy plush, for which its high lustre renders it suitable. Jute is also not infrequently used along with animal fibres, and it also serves to mix with hemp, though its low tensile strength militates against it.

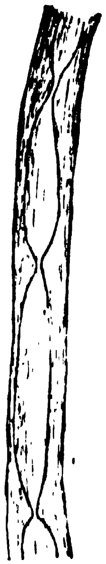

Fig. 5. Jute fibre.

Structure. In microscopic structure jute fibre exhibits a certain similarity to hemp and flax, inasmuch as the cells in the cross section are grouped polygonal and sharp cornered. On the other hand, the longitudinal view shows neither displacement nor striations, and the lumen is nearly as broad as the cell walls, or even more so, besides being strongly constricted at intervals a special characteristic of jute fibre. In consequence of the irregular thickening of the cell walls, it is advisable before examining jute under the microscope to treat it with alkali or chromic acid, which isolates the individual fibres.

Composition. Differing from other bast fibres, jute mainly consists of a compound of cellulose with lignine or other similar body, the compound being known as *bastose*. The specific gravity of jute is the same as that of hemp.

Chemical Behaviour. Jute gives the lignine reaction by taking a yellow stain with iodine and sulphuric acid, whilst aniline sulphate colours it dark yellow. When treated with chlorine the principal constituent, bastose, is converted into a compound, which, like cotton containing tannin, is stained a fuchsine red by alkaline sulphites. It may be distinguished from hemp by the red brown stain produced by concentrated nitric acid. Jute cannot be bleached with chloride of lime since it combines with the chlorine and yields an insoluble compound with the lime. Consequently, sodium hypochlorite must be used for bleaching.

Jute is usually dyed in an acid bath, though alum should be employed on account of the weakening effect produced on the fibre by mineral acids.

To impart a wool-like appearance to jute, the fibre is treated with strong soda lye (about 30° B.), then washed in water and rinsed with dilute acetic acid. The fibres then bear a very close resemblance to sheep's wool, and have a greater affinity for dye-stuffs than ordinary jute.

Ramie, Rhea, China Grass, Nettle Fibre.

Definition and Occurrence. For a very long time silky, soft, and extremely strong fibres, known under the above names, have been prepared in China and India from various species of nettle, particular importance attaching to the fibres from *Boehmeria nivea* and allied species. At present ramie and China grass are no longer considered as being distinct fibres.

Preparation.—Although there are numerous species of nettle yielding handsome fibres, only comparatively few are utilised, the stings of many of these plants having a very powerful action on the skin, and consequently rendering their manipulation very difficult.

Ramie fibres are obtained by stripping the fresh bast from the wood. In China, the freshly cut stems of the plant are first scraped to remove the rind, then left exposed to the sun for several days, after which the bast is thoroughly damped with the morning dew and is carefully peeled off, the fibres being then boiled and dried. As the bast will not easily strip except when the stalks are quite fresh, the successful preparation of ramie entails the employment of a very large number of hands in order to be able to treat the whole of the crop at once. To get over this difficulty, Sansone proposed to store the fresh-cut stalks in a solution of bisulphite in brickwork pits. Recently a great deal of trouble has been taken, especially in France and North America, over the construction of suitable decorticating machines for stripping the bast from the stalks in a quicker and more rational manner, this forming the most difficult part of the whole process.[1] When ramie is prepared in the form of single isolated cells, like cotton, instead of cell bundles like the other bast fibres, it is known as cottonised ramie, and can be spun to very handsome yarn. In Europe, ramie is bleached in the same way as cotton, and thereby acquires a dazzling whiteness.

Historical.—Ramie fibre has been prepared in India and China from time immemorial, and has also been found in mummy wraps. In more recent times ramie cultivation has been introduced into Egypt, Algiers, Spain, Italy, France, etc.

Commerce and Statistics.—It is only of late that ramie fibre has attained a certain degree of importance in Europe, and this would be still further increased were the difficulties in the way of its preparation removed.

China alone exports at present about 3500 tons per annum.

Chinese ramie, or China grass, is generally met with in commerce in the form of slightly yellow or greenish fibres up to about 8 inches long. It is only when the fibre has been bleached that it develops its valuable properties of gloss, whiteness, softness, and strength, which would render this fibre the most perfect of all those of vegetable origin, were it not for one great drawback, namely, that the surface of the fibre, instead of being smooth, is covered with a number of fine projecting fibrils. These greatly diminish the lustre of ramie fabrics, and are also the cause why ramie is not very suitable for the production of body linen.

Ramie is used in conjunction with other fibres; for example, it is spun along with wool, the resulting yarn being used as a weft in woollen-warp fabrics.

Structure.—Ramie fibre chiefly differs from the other vegetable fibres in the great length and breadth of the bast cells, which are up to 8 inches or more in length, and on the average about twice as broad as cotton. The fibre is very irregular longitudinally; in the wide parts it is ribbon-like, flat, and also exhibits frequent displacements and longitudinal and cross fissures. The axial twist noticed in cotton also occurs here.

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[1] For some years past ramie has been cultivated in Sumatra by a European company, the Faure decorticator being successfully employed.

The lumen is broad, the ends of the fibres are thick and rounded, and exhibit a linear lumen similar to that of hemp. In cross section the cells are mostly independent, very large, long and compressed.

Composition.—Ramie fibre consists of almost pure cellulose, without any lignification. The specific gravity is 1·51 to 1·52.

Behaviour Towards Reagents. Iodine and sulphuric acid impart a copper red to pure blue coloration, according to the degree of purification. Ammoniacal copper oxide gives a blue stain, the fibre swelling up greatly at first and finally passing entirely into solution. Aniline sulphate gives no coloration.

The intercellular substance connecting the bast cells has very low powers of resistance against reagents, a circumstance explaining the ease with which ramie fibres can be bleached.

Distinguishing Tests for the Various Fibres.

As may be easily gathered from the foregoing descriptions, there are two modes available for recognising and distinguishing the various vegetable fibres, viz. the microscope and chemical reactions. In employing the microscope, it should be remembered that the characteristic indications of a fibre are often lacking in places, or less frequently observable in some kinds, one instance of this being the spiral twist in the case of cotton. Consequently, the examination of a single fibre is insufficient, and must be extended to several throughout their entire length. Chemical reactions, or rather the characteristic colorations given by the different fibres with various reagents, are largely dependent on the concentration of the latter and on the purity of the fibre. Thus, for example, a highly bleached cotton twist often fails to give the characteristic reaction with ammoniacal copper oxide owing to the fact that the cuticle may have been removed in bleaching.

It is advisable to use reagents of a constant known strength. The usual solutions are prepared in the following manner:

Iodine Solution. A 1 per cent. solution of potassium iodide is completely saturated with iodine; this solution must be renewed from time to time.

Sulphuric Acid.—Three parts by volume of concentrated sulphuric acid are mixed with 1 part of water and 2 parts of perfectly pure glycerine; fresh acid must be added from time to time. This solution will then be of the right strength for examining fibres. When a flax fibre is treated therewith it does not swell up, but on the addition of iodine immediately gives a blue coloration, and not merely a pink or violet.

Zinc Iodochloride.—A concentrated aqueous solution of zinc chloride is added to a solution of iodine in potassium iodide, the following proportions being taken:—

1 part I.	30 parts $ZnCl_2$.
5 parts KI.	14 parts H_2O.[1]

As to which of these methods more quickly and readily leads to the desired result, this depends on circumstances. In many cases a simple macroscopical examination will suffice; but where absolutely reliable results are desired, the microscope is indispensable. Colour reactions must only be employed with care. In a few instances the end will be achieved quickest by a combination of macroscopical examination and the use of the microscope: for instance, when it is a question of detecting cotton in the warp of a linen fabric. It would take too much time to look at all the warp threads under the microscope, and a much quicker way is to select for closer examination such of the threads as appear to contain cotton.

In view of the great technical and commercial importance of distinguishing between flax and cotton, the question may be gone into in more detail. The examination can be performed in several ways, the first stage of all, however, being to free the test sample from dressing, by boiling it with water or treating it with warm soda solution. The most reliable tests to apply are the following:—

1. A small sample is soaked in oil and examined by reflected and transmitted light. In the former, the flax fibres appear dark, whilst in the latter they are pale and transparent. On the other hand, cotton is pale by reflected light and dark by trans-

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[1] This is the formula given in the literature, but the amount of iodine is really much too large.

mitted light, on account of the fact that the oil cannot displace the air imprisoned in the lumen of the fibre.

2. A sample of the fabric is treated with a warm aqueous solution of methylene blue, and washed. The flax fibres are stained dark blue, those of cotton light blue. This test, which can also be used on bleached goods, is the most reliable of the colour reactions.

3. A dry sample is laid for 1 to 2 minutes in concentrated sulphuric acid, and then washed with water. The cotton dissolves, leaving the flax fibres practically intact, so that this test forms a quantitative method of approximately determining the proportions of cotton and flax in linen union fabrics.

The differences between cotton and flax when viewed under the microscope may be assumed to be already known, and it will be sufficient to draw attention once again to the characteristic appearance of cotton fibre that has been treated with ammoniacal copper oxide.

In distinguishing flax from hemp, two important criteria come under consideration: (1) The lignine reaction, hemp being, as a lignified fibre, stained yellow by aniline sulphate, whereas flax is not; (2) the ends of the fibres are pointed in the case of flax, but thickened and often forked in hemp. As already mentioned in describing hemp, a low power (20 to 30) should be used first.

Jute is distinguished from flax by the lignine reaction, and from hemp by the nitric acid reaction (jute is stained red-brown, hemp a pale yellow). Under the microscope the chief distinctive characteristic of jute consists in its irregularly thickened cell walls, which cause the lumen to appear strongly constricted in places.

Finally, as regards the differentiation of ramie from other fibres, this presents no difficulty, owing to the great breadth of the ramie fibre.

4. Animal Fibres.

Silk, Wool, Goat Wool, Camel Wool, and Byssus Silk.

General Properties and Differentiation from Vegetable Fibres.—As their name implies, the animal fibres are of animal origin, and consequently do not, like the vegetable fibres, consist of cellulose, but of complex nitrogenous bodies of the protein class. In addition, the animal wools contain sulphur.

For the above reasons their behaviour is therefore very different in presence of the usual reagents and dye-stuffs. This difference is already apparent when they are simply moistened with water, which they take up less readily than the vegetable fibres, and which causes them to swell up to a smaller extent than the latter. The practical consequence of this behaviour is self-evident: the animal fibres, especially sheep's wool and goats' wool, require to be more strongly wetted than the vegetable fibres in the course of preparation for dyeing. Nevertheless, the animal fibres are much more hygroscopic than those of vegetable origin, *i.e.* they take up much more moisture when exposed to damp air.

The two classes of fibres also exhibit very important differences in their behaviour towards acids and alkalis.

The animal fibres, wools in particular, are more resistant than the vegetable fibres towards acids, a property on which the well-known method of separation, termed carbonising (*q.v.*), is based. On the other hand, they are much more susceptible towards alkalis, and on this peculiarity is based the determination of cotton and other vegetable fibres in mixed fabrics and wool substitutes. Consequently, special care must be adopted in treating animal fibres with alkaline reagents.

The carbonates of potash and soda should be used at temperatures not exceeding 50° C., even when in a dilute condition. Caustic alkalis, except ammonia, have an injurious action on animal fibres under all circumstances, though (see under silk and wool) in some circumstances stronger solutions are less active than dilute ones. Considerable difference also exists between the two classes of fibre in dyeing, animal fibres having a greater affinity for the dye-stuffs, especially the acid dyes; the same remarks apply with regard to mordants, a point that will be discussed later on.

In bleaching, the use of chloride of lime is inadmissible for animal fibres, owing to the corrosion produced. Finally, the behaviour of the two classes of fibre when burned is so divergent that this test offers a ready and reliable means of distinguishing between them. On setting light to a vegetable fibre it burns rapidly, and gives off a smell of burnt paper (which itself consists of vegetable fibre), leaving behind a loose white ash. Animal fibres, on the other hand, burn very slowly, give off a smell of burnt horn, and fuse to a small bead of hard porous carbon. Vegetable fibres can be quickly detected in association with animal fibres by warming the sample of fabric with dilute alkali, and examining it under the microscope after washing: the animal fibres will be found considerably swollen and transparent, the vegetable fibres scarcely swollen at all, and sharply defined. Again, if the sample be boiled for about a quarter of an hour in 8° B. soda lye, the animal fibres will dissolve; the residue is then examined, for the presence of vegetable fibres, by the combustion test and under the microscope.

To distinguish real silk from lustrous threads made from cellulose (artificial silk and mercerised cotton) the sample is heated in a solution of fuchsin that has been decolorised with ammonia. The real silk fibres alone are stained; but the proportion of ammonia must not be too high, or the silk will not take up the dye, and, on the other hand, too little ammonia leads to the staining of the cellulose fibres.

Animal wools are distinguished from all other fibres by containing sulphur, and, if boiled along with a solution of lead oxide in soda lye, they will turn black, owing to the formation of lead sulphide.

Silk.

Morphologically, silks are the simplest, and in their other properties the most perfect and the most highly prized, of the textile fibres. The chief difference is in point of structure, since whereas the vegetable fibres are organised and are products of vegetable growth, and wool also grows as an organised structure out of the skin of the sheep, silk is a solidified secretion of the larvæ of various moths, and, consequently, is devoid of cellular structure. According as silk is obtained from the larvæ of wild moths or the cultivated silk-worm, it is termed wild or true silk. These two varieties differ in so many respects as to necessitate entirely separate descriptions, the true silk being taken first on account of its far greater value.

True Silk.—The life-history of the true silk-worm, *Bombyx mori*, is identical with that of the wild silk-worms, and may be briefly described as follows:—

The perfect insect neither takes nourishment, nor does it produce silk, the sole object of its short existence being the reproduction of the species. From the egg laid by the moth is hatched the sexless form of the insect, the larva, and from this in turn proceeds the pupa or quiescent intermediate form. In order to protect the unharmed pupa from external influences, the larva, before passing into the pupal stage, surrounds itself with a casing or cocoon of silk fibre, which cocoon forms the raw material for the manufacture of silk.

Silk-Worm Breeding.—This pursuit is carried on in establishments known as "magnaneria," and also as a home industry. The first condition for founding an establishment of this kind is the planting of a sufficient number of mulberry trees, the true silk-worm feeding exclusively on mulberry leaves and requiring an abundant supply of these to enable it to produce fine cocoons. A deficient food supply causes the worm to produce either a smaller quantity or inferior quality of silk. 14,000 larvæ, the cocoons of which will eventually yield from 3 to 4½ lb. of silk, will consume during their lifetime about 9 cwt. of leaves, from which figures it can easily be seen that very large mulberry plantations are required for production of silk on a large scale.

When fresh, the eggs of the silk-worm are yellow, dry, whitish-grey, and resemble ordinary poppy seeds in form and size, about 16,000 being required to weigh a lb. For hatching, they are spread out on sheets of paper in well-ventilated and slightly damp chambers, the temperature of which is gradually raised in ten to twelve days to 60°, 64°, 68°, and 77° Fahrenheit; at this temperature the larvæ, which are very small, motile, and covered with blackish hairs, emerge from the egg, and are transferred without delay to frames covered with white paper. Only those from one hatching are put on the same frame, in order that they may all subsequently spin at the same time. They are now fed with fresh, dry, mulberry leaves cut up, and, in proportion as the larvæ grow, they must be transferred to larger frames. Uniform temperature and moisture, care, cleanliness, and abundance of fresh food, are indispensable conditions for obtaining strong healthy worms and good quality silk.

The silk-worm is an extremely voracious animal and grows at a correspondingly rapid rate, until it attains three to four inches in length and weighs about one-sixth of an ounce. At this stage it is of a floury whiteness, or spotted with brown and black, and its body is divided into ten segments, the foremost of which is somewhat enlarged, and carries the head and true legs. It is interesting to note that these legs are of the same colour as the silk that will be subsequently supplied by the worm, *i.e.* white, yellow, or greenish. During its lifetime the silk-worm sheds its skin four times, and is at this period particularly susceptible to external influences. After the fourth shedding, the larva lives another eight or ten days, whereupon it ceases to eat, evacuates the contents of its stomach, and moves restlessly about. It is now transferred to dry mulberry or other twigs, where it at once begins to spin, discharging from its under jaw a thread (silk), with which it first forms a loose network or bed, and then begins to spin the true cocoon. This it does by moving its head to and fro, and winding the exuding silk thread around its body in a very regular manner. In a short time it is completely enclosed, and the cocoon is finished in about four days. Inside the cocoon the larva develops a final skin, and is converted into the pupal state. The shape of the cocoon differs according to the sex of the future insect, the females being oval, whilst the males are a little smaller, more cylindrical, and slightly constricted in the centre. They average about 1·2 inches long, and 0·6 to 0·78 inch across. When fresh they have the following approximate composition:

	Per cent
Water . . .	68
Silk .	14
Waste .	0·7
Pupa . .	17

They are formed of a single, seldom interrupted, double fibre, which is strongest and most uniform at the centre and varies in length from 400 to 3300 yards. The innermost layer of all, surrounding the pupa, resembles a thin skin of parchment. After about ten days the cocoons are collected and sorted. Double cocoons, produced by two larvæ spinning themselves in together, or cocoons exhibiting other peculiarities, must be sorted out, being unsuitable for the manufacture of silk in the ordinary manner. Moreover, a certain number of male and female cocoons are set aside for the purpose of reproduction, all the rest being sent to the reeling house.

The cocoons intended for breeding are placed in a chamber heated to a temperature of 68° F., where, in about twenty days after the completion of the cocoon, the moth, which in the meantime has become perfectly developed, moistens one end of the cocoon with saliva, pushes the threads apart, and crawls out. The wings are kept in constant motion until they have expanded to their full size. The moth is floury white in colour and immediately begins to pair, its life terminating as soon as the eggs have been laid. The eggs are carefully dried and stored until the following spring in a cool, dark, dry place. 1 grm. (15 grains) of eggs will yield over 11,000 larvæ = 3 to 5 lb. of finished cocoons.

Diseases of the Silk-Worm. Silk-worm breeding is a difficult operation, entailing great care and attention. Moreover, the larvæ are subjected to a number of diseases. At the commencement of the sixties, two highly devastating epidemics made their appearance in the silk-worm industries of southern Europe and India. Their origin was investigated by Pasteur and others, and traced to fungoid growths developing in the bodies of the larvæ.

The Chinese and Japanese breeding establishments are, it is true, unaffected by this disease; but, on the other hand, the Japanese industry suffers from another disease caused by a species of ichneumon fly, which bores holes in the young silk-worm and deposits its eggs within the body of the latter.

Silk Manufacture.—The first task consists in killing the pupæ in the cocoons. It is effected in one of two ways, either by heating the cocoons in an oven for two or three hours at 60 to 70° C., or by exposing them for about ten minutes to the action of steam. The cocoons are then sorted, the best and finest being used for the production of so-called organzine, whilst the inferior grades are used for making trame. In weaving silk fabrics, the organzine fibres are used as warps, and trame as wefts. The silk threads forming the cocoons are next reeled, for which purpose they are first steeped in hot water in order to soften the gelatinous matter surrounding the threads, and are placed in a basin of lukewarm water. The attendant who looks after the reeling then works the cocoons about with a small brush of twigs in order to find the ends of the threads. Several ends are then united to a single thread and two sets of compound threads of equal thickness are passed separately through perforated agate guides, and, after crossing at one point, are again parted, passed through a second pair of guides and thence on to a reel which is worked at a speed of 800 to 900 revolutions per minute. The mucinous matter, softened by the hot water, causes the loose cocoon threads to stick together and form the simplest class of raw silk thread—grège.

Reeling is a work requiring the greatest attention in order to prevent tearing the silk during the search for the ends, and also to secure uniform thickness in the reeled threads. It is a matter of considerable difficulty, and a good deal of silk gets broken during the former operation.

Recently an automatic silk reeling machine was invented by an American, E. W. Serrell.

Working up Waste Silk.—The silk forming the outer layer of the cocoon, and also that of double cocoons, perforated, burst, or otherwise defective cocoons, and the broken ends in reeling, constitute the so-called waste or florette silk. These cannot be worked up by reeling, but have to be treated by Lister's process—namely, scouring with soda and soap, then combed or carded in suitable machines like cotton, and finally spun. There are two classes of waste silk, namely, florette and bourette; the former consists of the better and longer fibre and is prepared in a manner more similar to worsted, whilst the inferior bourette is worked up in the same way as carded yarn.

At the present time florette spinning forms an important branch of the silk industry; nevertheless it is inferior in value to reeled silk.

Historical. The historical data on the subject of silk are so comprehensive and interesting as to deserve mention in the present work. China is the home of the silk industry, and it has been known there from time immemorial that certain larvæ contain a secretion from which very durable threads can be produced. At one time these threads were used in making strings for musical instruments, and they are even now employed as fishing lines.

The discovery that fabrics could be prepared from cocoons is attributed to Te-ling-Shi, wife of the Emperor Hoang-te, about 2650 B.C. This monarch is also said to be the first to wear silken garments, and his lady was, after death, raised to the rank of a deity. From that time the Chinese silk industry has been closely connected with the history of the country. It was placed under royal protection, and for a long time formed a monopoly of the monarch and nobility.

The ancient Greeks were also acquainted with Chinese silk, and held it in very high estimation. Thus, according to a calculation made by Pariset in the time of the Emperor Aurelianus, one pound of raw silk was worth about £24, and one pound of purple dyed silk four times that amount. This price, however, subsequently fell away to a great extent, so that in the fourth century all classes in Rome wore silken garments. Florette silk from the wild Assyrian moth was also known to the ancients and highly prized, namely, the so-called Bombykia, from which the Coan fabrics were manufactured. In India, Persia, and Japan the cultivation of silk was introduced from China, though it is undeniable that many of the inhabitants of those countries were already acquainted with and made use of this fibre. In Europe, silk was long regarded as a vegetable product. It was introduced during the first half of the sixth century of our era, and it is recorded that about this period the first silk-worms were brought to Byzantium, concealed in hollow bamboo rods, by two monks. The industry thus founded afterwards spread to Greece, Spain, and Italy.

Commerce and Statistics.—At the present time the cultivation of true silk is carried on (with great care) not only in its Asiatic home, in China, Japan, and India, but in southern

Europe, Italy, the south of France, Greece, and the Levant. China and Japan are the chief sources of supply of eggs for the European silk-worm industry, the diseases already mentioned having devastated the breeding establishments in southern Europe, and India. Nowadays silk culture is making advances in every direction, e.g. in Bulgaria, China, and Japan. Although far from equalling European silk in fineness and regularity, the Asiatic silk predominates in point of quantity, and the Chinese production is increasing largely. The total production of silk throughout the world is estimated at 33,000 tons, of which China produces about one half.

Physical Properties. Raw silk is usually yellow to white in colour, though occasionally of a faint greenish tinge (Japanese silk), and only after being boiled and subjected to various mechanical operations does it acquire those properties for which it is so highly esteemed.

Scoured silk is distinguished by high lustre, strength, toughness, and elasticity, the tensile strength being almost as great as that of iron wire of equal thickness. Unfortunately, for many years past, both white and coloured silk fabrics are only found in commerce in a heavily loaded condition, which greatly impairs their tensile strength. The elasticity is also high, a dried silk thread being susceptible of extension by one-seventh to one-fifth of its original length. These two properties mainly reside in the outer glutinous layer and are diminished by about 30 per cent. in scouring. Moreover, immoderate loading (in black dyeing) deprives the silk of a good deal of its valuable properties. When dried silk is moistened it contracts by about one-seventh, and the same also occurs in dyeing.

Silk is a poor conductor of electricity, and when subjected to friction remains electrified, a circumstance which may cause a deal of mischief in the manufacturing process; this defect, however, can be obviated by keeping the factory atmosphere moist. A property possessed by silk alone of all the textile fibres is that of emitting a crackling sound (scroop) when compressed. This property, however, is not originally present in the silk, but is acquired after immersion in an acid bath. No proper explanation of this phenomenon has yet been discovered, but it is assumed that the acid roughens the surface of the fibre, and that the noise results from the increased friction thereby ensuing when pressure is applied.

Production and Structure of the Silk Fibre.—The silk fibre is produced in two glands along the inside of the body of the silk-worm, which glands are in the shape of convoluted cylindrical threads, and occupy a considerable amount of space in the full grown larva. The glands consist of three principal portions (Fig. 6): (1) the part *a*, *b*, where the silk is probably formed; (2) the broader part *b*, *c*, wherein the silk is probably stored; and finally (3) the capillary tube *c*, *d*, where a partial hardening of the silk occurs. In this manner two threads are simultaneously formed, which unite at *d*, and issue from the silk-worm's head in the form of a double thread, which only becomes thoroughly hardened on exposure to the air. If the silk gland be cut through at the thickest part, it is found to consist of two distinctly separate parts, an internal transparent layer, and an external stratum which is colourless, greenish, or yellow, according to the breed of the silk-worm, and occupies about one-fourth of the total volume. As in the scouring of raw silk, which dissolves the sericin, an almost identical loss

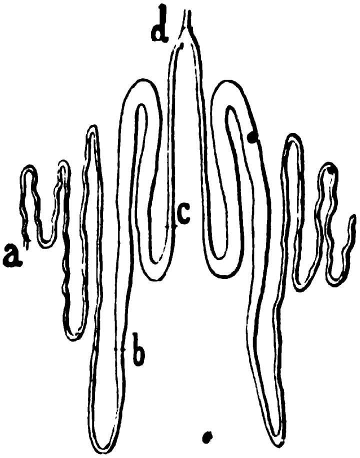

FIG. 6.

in weight occurs, it is concluded that this is formed simultaneously with the substance of the silk.

In harmony with this method of formation, the silk fibre exhibits under the microscope the appearance of a clear cylindrical double thread, enclosed in a cloudy integument. As is

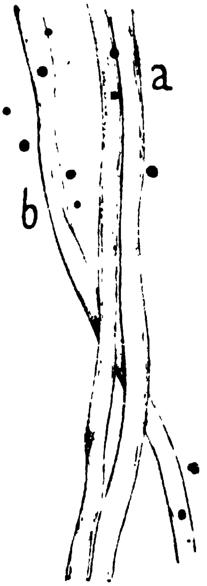

FIG. 7.
(a) Raw silk thread.
(b) Scoured silk.

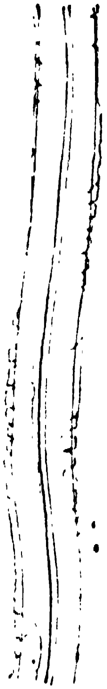

FIG. 8.
Florette silk.

shown in Fig. 7, the two threads stand apart in places, and in scoured silk are entirely separated; consequently, whilst raw silk consists of a double thread, the scoured silk is single.

Florette silk can be recognised by the irregular appearance of the external layer (Fig. 8).

The structure of silk is, however, not so simple as the microscopical picture would lead us to expect; and, in fact, the fibre is composed of a number of smaller elements or fibrils, connected together by a small quantity of matrix. This can be concluded from the following facts

When a silk fibre, exhibiting a slight striation, is treated with chromic acid under the microscope, the striation is rendered more clearly defined. More conclusive evidence is, however, afforded by the behaviour of the fibre in presence of moderately strong sulphuric acid assisted by heat, since if, after impregnation with this acid, the silk be dried and then heated to 80° to 100° C., it will be found, on careful examination under the microscope, to be entirely disintegrated into fibrils, separated by the preceding treatment. A similar, and still more decisive, proof is afforded by "lousy" silk (see later, under Decortication).

Chemical Composition. As already stated, the silk fibre consists of two portions, the outer layer or *sericin*, and the real substance of the silk, or *fibroin*, the latter constituting about two-thirds of the total material present in the raw silk

Sericin is a substance soluble in water and resembling ordinary gelatine, though, when boiled for some time with dilute sulphuric acid, it furnishes decomposition products differing from those yielded by gelatine.

Fibroin is entirely insoluble in water and is classed along with the proteids. On comparing the empirical formulæ of fibroin and sericin, the following simple relation is found to exist between them

$$\underset{\text{Fibroin.}}{C_{15}H_{23}N_5O_6} + O + H_2O = \underset{\text{Sericin.}}{C_{15}H_{25}N_5O_8}$$

It is therefore possible that sericin is produced from fibroin, an assumption that would seem to be justified by the fact that when scoured silk, entirely freed from sericin, has been left for some time exposed to damp air, it loses in weight on being subsequently boiled in water.

According to E. Fischer and A. Skita, however, this hypothesis is untenable, their researches having shown that, whilst fibroin and sericin are of the same qualitative composition (both containing the same fission products, tyrosin, glycocoll, alanin, cerin, arginin), the percentage proportions of these constituents are different in the two substances.

In addition to the foregoing substances raw silk also contains water, and, in small amounts, fat, wax, and pigmentary matter.

The specific gravity of both raw and scoured silk is 1·34 (Vignon).

Behaviour Towards Reagents. Silk will stand a temperature of 110° C. without undergoing any alteration, but rapidly decomposes on being heated to 170° C. When held in a flame it burns, and, like wool, appears to fuse, without, however, disengaging such an unpleasant smell as is evolved by the latter.

When in the pure state, silk is highly resistant towards putrefactive agencies. It is very hygroscopic, absorbing as much as 30 per cent. of water when exposed to damp air. Owing to this circumstance, and the fact that it is a very expensive material and is sold by weight, it becomes necessary to determine the actual weight of silk in each bale, an operation that is performed in silk conditioning houses, which establishments will be described later on.

In addition, silk is a very porous substance, and has a high adsorptive capacity for all kinds of bodies, *e.g.* alcohol, acetic acid, tannin, sugar, etc. Its capacity for adsorbing dyestuffs is greater than that of any other textile fibre, and is even exhibited at the ordinary temperature. Furthermore, certain salts, used as *mordants*, are adsorbed in large quantities by silk, a phenomenon on which is based the operation known as loading or weighting silk.

Warm dilute acids dissolve the sericin, but leave the fibroin untouched; concentrated acids, however, exert a destructive action. Cold acetic acid dissolves out merely the colouring matter of raw silk, without attacking the sericin, though when heat and pressure are applied the silk dissolves in this acid.[1] Concentrated nitric acid stains silk a beautiful yellow, xanthoproteic acid being formed. This coloration is deepened by alkalis but lightened by acids, and is destroyed by a boiling hot solution of stannous chloride. Formerly this colour was utilised industrially.

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[1] Concentrated strong acids cause real silk to contract by 30 to 50 per cent., a property which can be utilised for the production of crêpe effects. Tussah silk, however, does not shrink under this treatment.

Concentrated basic zinc chloride dissolves silk to a viscous solution. A concentrated acid solution of zinc chloride also readily dissolves silk, and the solution can be diluted with water without precipitation being produced. When the liquid is dialysed, to completely remove the acid, an aqueous solution of chemically altered sericin is obtained. This operation, though undoubtedly interesting, does not, however, seem capable of any practical utilisation, inasmuch as the bulk of the sericin is thrown down during dialysis, and in no case is the solution entirely free from zinc, however prolonged the operation may be. On evaporating the solution to dryness, a yellow substance is obtained, which resembles colophony in appearance and is no longer soluble in water.

Dilute alkalis diminish the gloss of the silk, and when moderately concentrated dissolve the material in the warm. In presence of glucose, silk can be treated with even highly concentrated alkalis, but, of course, only in the cold. The Badische Co. has a patent, based on this circumstance, for scouring fabrics containing raw silk and raw cotton. Ammonia exerts no appreciable influence in the cold, and soap acts merely as a solvent of sericin, though, after prolonged exposure at boiling heat, the fibroin also is attacked.

Silk is soluble in both ammoniacal copper oxide and ammoniacal nickel oxide, but differs from cotton in not being reprecipitable by additions of salt, sugar, etc. This solubility in ammoniacal nickel oxide as also in zinc chloride can be utilised as a quantitative test for silk in mixed fabrics, the following method being adopted, according to Richardson:—

Twenty-five grms. of crystalline nickel sulphate are treated with caustic soda to throw down the oxide, which is then carefully washed and rinsed by the aid of 125 c.c. of water into a 250 c.c. flask, which is filled up to the mark with ammonia (sp. gr., 0·88), the liquid being then employed for treating the tissue under examination by boiling them together for ten minutes under a reflux condenser. The silk is completely dissolved, and the cotton loses 0·8 per cent. in weight.

For silk and cotton goods the following method is, however, preferable:—

A solution is prepared of 1000 parts fused zinc chloride and 10 parts zinc oxide in 850 parts of water; and the fabric, after being boiled in this solution for one minute, is freed from zinc by washing with hydrochloric acid (1 per cent. strength). Under this treatment 0.5 per cent. of the cotton (or 1.5 to 2 per cent. of wool, if present) is also dissolved.

Wild Silk. In China, Japan, and India, the home of the true silk-worm, there are also found insects belonging to the nocturnal peacock moth family, which not only have the same life-history as the true silk-moth, but also furnish a very similar class of silk, though differing therefrom both morphologically and in point of behaviour towards chemical reagents.

Although the manufacture of fabrics from the cocoons of wild silk-moths was practised in the aforesaid countries from the earliest times, it was only about 1860 that in consequence of the silk-worm disease, the attention of European silk manufacturers was drawn to this material.

The chief reason for this is to be sought in the fact that the wild silk-worm makes several pauses when spinning the cocoon, the consequence of which is that the cocoon is composed of several threads difficult to disentangle and therefore unsuitable for reeling. However, since Lister's method of working up waste silk was applied to wild silk, the cocoons of these wild spinners have become an important factor in the European silk industry, plush and velvet in particular being now made in large quantities from this raw material.

The main advantages of wild silk are:—(1) Its greater durability, owing to the greater thickness of the threads, though, in consequence of the method of treatment pursued, the true silk threads are stronger in the finished fabric; (2) greater cheapness and productivity, inasmuch as the wild silk-worms do not require to be cultivated, but spin their cocoons on trees in the open. Moreover, the cocoons are larger and yield more silk than those of *Bombyx mori*, and many of them bring up several broods in a season (2-8), whilst *Bombyx mori* gives only one crop in the year.

On the other hand, apart from the inferior regularity of the cocoons, the wild silk-worms exhibit the disadvantage of furnishing a silk that is always more or less highly coloured and is very difficult to bleach. For this reason wild silk is mostly spun and woven in an undyed -natural condition. There is, however, some hope that this difficulty can be surmounted, since, according to the observations of O. N. Witt, wild silk is always colourless when first formed, but is afterwards coloured by the secretion employed by the worm to moisten the spun thread. The coloration thus imparted depends on the plant on which the larva has been fed, and is darker in proportion as the plant is richer in bodies that furnish pigments on exposure to the air. Hence, if the worms during the latter stage of their existence be fed on plants incapable of furnishing such pigments (tannin, etc.), perfectly white silk will be obtained.

On this point practical experiments on a large scale have been successfully carried out, Major Coussmacker having obtained perfectly white cocoons in India by feeding the larvae of *Antheraea mylitta* in a suitable manner. This result is the easier of attainment in that, unlike the true silk-worm, the larvae of the wild spinners are not restricted to one source of food supply, but easily stand a change of diet. No technical success, however, has yet been obtained.

The chief wild spinners are

Antheraea mylitta, which occurs all over India, and yields the most valuable of all wild silks, *viz.* Tussah silk.

The Eria spinner, *Attacus ricini*, met with in tropical Asia, also in North and South America, yields a very handsome, almost white product, that is daily growing in value. Special mention should be made of one individual of this tribe, *viz.* *Attacus atlas*, the largest known moth, which produces open cocoons, from which the so-called Fagara silk is obtained.

Antheraea Yamamai, the Japanese oak moth, furnishes a pale green, very handsome silk, which is the nearest to true silk in character, and is highly esteemed.

Antheraea Pernyi, the North China oak moth, yields a silk that is very largely exported under the erroneous designation of Tussah silk.

Tussur or Tussah Silk.—This, being the most important and best known of all the wild silks, will be described more particularly.

The moth (*Antheraea mylitta*) from which this silk is obtained occurs throughout the whole of India and Southern China, and has been bred regularly in the former country from time immemorial, the industry being carried on by organised castes, and attended with numerous religious ceremonies. According to the Hindoo faith, the Tussah moth is the incorporation of the god Shiva, and the silk-worm breeders must abstain from eating meat, washing, and shaving during the whole time the larvae are growing and spinning.

The Tussah cocoons are attached by their stems on to twigs, and are reeled, an operation that is very carelessly performed in India. Sometimes the cocoons are brought to Europe, but in that event are not reeled, being spun instead.

Tussah silk exhibits all the aforesaid advantages and defects of the wild silks in general. Chinese Tussah, which is frequently confounded with the Indian variety, is darker in colour and inferior in lustre and beauty.

When examined under the microscope, Tussah exhibits a highly characteristic appearance, differing greatly from that of true silk (see Fig. 9), the fibres showing strong striation, and being apparently much constricted in parts. The very distinct striations are caused by the numerous very fine fibrils of which each fibre is composed. Unlike true silk, the fibre is not of circular cross section, but of elongated quadrilateral form.

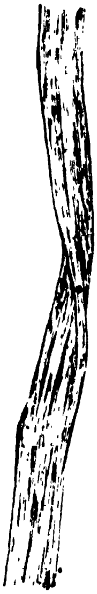

Fig. 9.

In presence of reagents, acids and alkalis in particular, Tussah silk behaves very like true silk. It is, however, much more resistent than the latter, especially towards solvents, so that the two kinds of silk can be separated in a fairly accurate quantitative manner, for instance, with ammoniacal nickel oxide in which Tussah silk is only very slightly soluble.

Tussah silk contains 16 to 30 per cent. of sericin, which, however, on account of its resin content, cannot be used in the preparation of the dyeing bath.

The other wild silks behave very much the same as Tussah silk.

Byssus Silk.—This fibre, which morphologically and chemically is nearly allied to true silk, is the product of certain mussels which are found in Sicily, Sardinia, and Corsica, and spin a long silky thread, for the purpose of attaching themselves to the rocks at the bottom of the sea.

This fibre is golden brown in colour, lustrous, soft, and elastic. In former times it was extensively collected, and employed in the manufacture of the highly prized Byssus garments; but at the present time it is not much used, its collection being attended with considerable difficulty. From a chemical point of view, it differs from other silks in that it merely swells up when treated with acids, alkalis, or ammoniacal copper oxide, without passing into solution.

ANIMAL HAIRS.

The skins of all warm-blooded animals are covered with a protective coating of horny cellular structures, which, in the case of mammals, assume the form of hair, and constitute the feathers of birds.

These structures are elaborated in special glands in the skin, and protrude through the epidermis in proportion as they increase in length in consequence of cell multiplication.

Animal hairs are the most complex, morphologically, of all textile fibres, and, after silk, are the most perfect. In point of chemical behaviour and conduct in presence of reagents, they closely resemble silk, and therefore may be classed along with the latter in one group—that of the animal fibres as contrasted with the fibres of vegetable origin.

Chief in importance among the animal fibres is—

Sheep's Wool.

Wool is the name given to the fibrous substance secreted by the skin of the sheep, and forming the hairy covering or fleece of the animal. This covering is composed of several similar elements, whose anatomical structure exhibits different degrees of development.

In the main the fleece of the sheep consists of body hairs and true wool hairs, the latter being thin, soft, and curly, and possessing the valuable property of felting, whilst the body hairs are thicker, darker in colour, and for the outer third of their length at least, stiffer and sharply tapered

In a few parts of the body, on the legs and head, of the animal there occurs a third kind of hair, *viz.* bristles, least of all endowed with the valuable properties of sheep's wool.

The fine wools of commerce are chiefly composed of only one of the above classes of hairs, *viz.* either body hairs alone or solely of true wool hairs; whilst common grades, on the other hand, form mixtures of both.

It is certain that the article we now regard as typical wool is not a really natural product, but one that has been gradually evolved in the course of many centuries of selection. Even at the present time there still exist two breeds of sheep, the Corsican moufflon and the argali, found in Asia and America, in whose hairy coats the valuable properties of sheep's wool are merely suggested. Moreover, it can be clearly observed in the domestic sheep that improvements in the breed by suitable selection produce a corresponding improvement in the wool. Consequently, the wools of the highest breeds consist almost exclusively of true wool hairs; though even in the finest wools may be found body hairs, which must be ascribed to atavism, *i.e.* a reversion to the original type of hairy covering.

The circumstances influencing the quality of wool and the percentage of body hairs therein are exceedingly numerous, chief among them being race and climatic conditions. Thus, for instance, in the hot, dry countries of Central Africa the proportion of wool hairs, in even the best breeds of sheep, steadily diminishes, and that of the body hairs as regularly increases. Conversely, the climate of Australia is so excellently adapted for wool-growing that even the poorest breed of sheep will produce a good wool in a few years time there.

Again, the fodder supplied to the sheep has a great influence on the quality of the wool. Grass from chalky soils produces a coarse wool, whilst that from rich, loamy soils gives fine silky fibres. Finally, the quality is influenced by the age and health of the sheep, and also depends on the part of the body on which it grows.

It is worthy of mention that the sheep producing the finest wool yield poor mutton.

Collection. The wool of the sheep is mostly obtained from the living animal by shearing—an annual operation. The amount of wool furnished by an individual sheep, of course, varies considerably, and depends mainly on the breed and sex, the male merino yielding about 8 lb. at a shearing, the female only about 5 lb. Taking the general average, the yield per head varies from 3½ lb. to 13 lb., though this is exceeded by some breeds—the Argentine ram, for example, occasionally producing a fleece weighing 40 lb. and upwards.

Wool that is cut from carcases or separated from the fells by liming, is known as tanners' wool, and is always inferior to the shorn fleece, especially when obtained by liming.

Historical, Commerce, and Statistics.—In Western countries wool has been used from very early times, whereas in Asia, the conditions being less favourable for sheep breeding, the article has always played a less important part, though the hair of certain goats, distinguished for its special lustre, has been there woven into fine fabrics from time immemorial.

The home of the sheep-breeding industry in Europe is Spain, where the indigenous merino sheep has been bred for its wool from very early times. In the Middle Ages the Spanish woollen industry was in a thriving condition, and the Moors devoted special care to the breeding of merinos. Subsequently the industry languished, but has recently revived. At first the Spaniards protected the breeding industry with extreme jealousy, and the exportation of a live merino sheep was prohibited under pain of death. This attitude, however, could not be maintained permanently, and, since the year 1723, merinos have been repeatedly exported to other countries, with beneficial results in every instance. Specially important for the breeding of sheep in Europe was the introduction of the merino into

Saxony in 1765, the Saxon Electoral breed now furnishing the thinnest and finest known grade of wool.

The introduction of sheep-breeding into Australia and New Zealand has been attended with the most successful results. Australia possesses no native breed of sheep, and it was only towards the end of the eighteenth century that the first sheep were sent over. The originally coarse, useless hair of these animals soon developed into good wool under the favourable influence of the Australian climate, and subsequent crossings of the breed with good English sheep brought about additional improvement, which was still further heightened by repeated crossing with merinos, so that at the present time the Australian sheep furnishes a wool ranking with the very best merino.

In South America, also—especially in Chili and the La Plata States—sheep-breeding has long been pursued on a large scale; and in North America the cultivation of wool has latterly made great strides, and will probably ere long attain considerable importance.

About fifty commercial grades of wool are known, chiefly divided into two principal classes—long and short staple, according to the length of the component fibres. To the latter class belong all wools measuring 1 to 1½ inch in length, those between 3½ and 6 inches being classed as long staple. The latter are treated by the combing process, and are used for making worsted fabrics; whilst the short wools are carded for spinning in the production of woollens.

With regard to the wool-production of the various countries, it must be admitted that, notwithstanding the increased activity in the woollen industry in Europe, the output of wool in that continent is on the down-grade, owing to the more favourable natural conditions prevailing in extra-European lands, and consequently the import of wool into Europe is constantly increasing. About half the total output of raw wool produced in Europe is grown in Russia.

The trade in extra-European wool is almost entirely in English hands, though latterly a share of the trade has been acquired by Belgium. Accurate statistics of production in the several wool-growing countries are difficult to obtain, European wools being occasionally brought into the market in a partly cleaned condition, whereas the extra-European article is always sent over in the grease (unwashed). The total production for the whole world may, however, be estimated at about 1,000,000 tons per annum.

As regards the woollen manufacturing industry, in this respect Europe is far ahead of any other countries, and the chief place of all is occupied by Great Britain.

Composition of the Fleece.—The term fleece is applied to the entire hairy coating of the sheep, including all impurities. It is composed as follows:—

Fibres	15—72	per cent.
Yolk (wool fat)	12—47	,,
Water . . .	4—24	,,
Dirt	3—24	,,

In addition to the hairs already mentioned, the fibres contain shorn hairs, recognisable by their clipped extremities when viewed under the microscope.

Structure.—Wool has the most complex and interesting structure of any of the textile fibres hitherto mentioned.

When a fibre of wool is examined under the microscope it is seen to consist of three parts, distinguished respectively as the scaly epidermis, the cortex, and the medulla or pith. The outer scaly epidermis is composed of thin horny scales lying one above another like the tiles on a roof. In the finer qualities of wool a single scale is generally sufficient to entirely surround the wool hair, so that the latter seems to be formed of a number of cups set one within another (Fig. 10, *b*), the upper edge of each scale being also generally projecting, ragged, and serrated. These scales form the chief external characteristic of sheep's wool, and render its detection under the microscope an easy task. They are, however, not always so well developed as the specimen given in Fig. 10, *b*; being in many instances less clearly visible, and in some merely present as faint broken lines (see Fig. 10, *a*). In other cases they may even be entirely absent in places, as, for example, in the wool of several breeds of country sheep where the scales are invisible for some distance from the tip of the fibre, or in wool taken from a piece of cloth which has been put through a finishing process that has stripped the scales off to a greater or smaller extent; and, even in some of the finest wools, the scales are occasionally very imperfectly developed near the tips. In the case of body hairs the scales are far smaller, and in no instance does a single scale surround the entire hair (Fig. 16 c).

On the structure of these scales depends one of the most

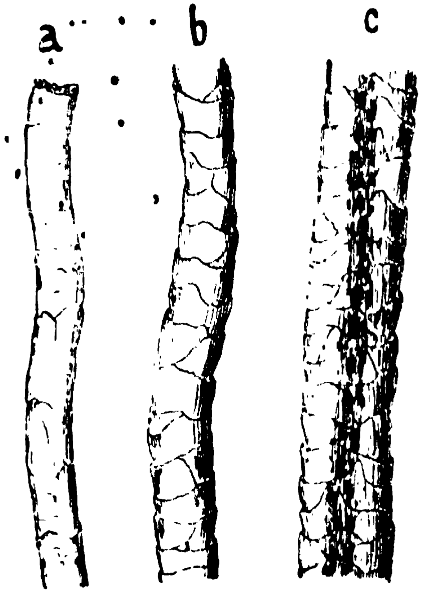

Fig. 10

valuable properties of wool, *viz.* the felting or shrinking power. This is due to the circumstance that, when the wool is soaked in certain solutions (*e.g.* soap), and subjected to pressure and friction, the individual scales engage one in another so that they can no longer be separated without breaking. On this behaviour is based the operation of fulling or milling woollen cloth. This explanation of felting property is in perfect harmony with the fact that body hairs, and, indeed, all other hairs with less fully developed scales, are harder to full than wool. Cotton, of course, will not felt, so that when a fabric containing both wool and cotton is milled, the former alone shrinks and the fabric acquires a crinkled appearance (crêpe effect).

Two other properties of wool also depend on the nature and arrangement of the scales, namely, the lustre of the fibre and the degree of facility with which it will absorb water and dye-stuffs. Wool, with scales that either lie down flat or project only very slightly, always has more lustre than that wherein the converse conditions prevail. Some common grades of wool have very hard scales, which tightly encompass the hair and greatly retard the penetration of water and dye; such wools must therefore be well wetted before dyeing.

The second or cortical layer of the wool-fibre consists of small spindle-shaped cells which give the wool its strength. These cells are visible, when viewed longitudinally under the microscope, as long striations, especially when the wool has passed through the finishing process.

Finally, the third or central layer, the medulla, is of far less importance than the other two, since it is entirely absent in the very best kinds of wool (merino). In fact, the dimensions of this medulla afford an indication of quality, since while the coarse body hairs have a broad medulla, and can thus be distinguished from the fine wool hairs under the microscope, the quality of the true wool hairs varies inversely with the amount of medulla they contain. The presence of this pith is a cause of weakness in the fibre, and therefore it gradually disappears in proportion as the wool is improved.

Microscopical examination plays an important practical part in the case of sheep's wool, since it forms the best means of distinguishing between the different kinds of wool, and also of differentiating between body hairs and true wool, the former being readily recognised by their well-developed medullary layer and small scales. Tanners' wool that has been removed from the pelt by liming can be detected by the presence of hair-root sacs, which are never found in the shorn fleece. Moreover, the microscope forms the best means of detecting the peculiar malady known as "stocks," and probably due to mouldy growths, which infests wool or woollen cloth that has been stored for some time in warm, badly ventilated rooms whilst in a damp state, especially if this dampness be due to alkaline liquids or contact with decaying wood. The malady is most frequently encountered in woollens dyed with indigo, and generally takes the form of small light-coloured spots distributed over the surface of the goods. The view that the mould eats away the dye is, however, erroneous (except, as was shown by Kalmann, in the case of vat-dyed blue wool), and it is really the fibre that is attacked and rendered brittle, the result being that it drops away and leaves a spotty mark. When the corrosion has proceeded sufficiently far, its effects on the fibre are clearly visible to the naked eye, and if a portion be examined under the microscope, a very peculiar and characteristic appearance will be detected (see Fig. 11), *i.e.* that the scales on some parts of the hairs, and especially at the tips, have disappeared, leaving the spindle-shaped cells of the cortical layer protruding like the hairs of a brush, whilst some of them have become detached

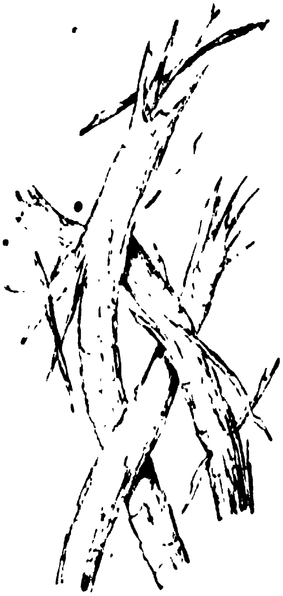

FIG. 11

altogether and can be seen lying upon and between the wool hairs. In other places they stick out from the side of the wool hairs like so many tufts.

Some skill is, however, required in detecting this characteristic appearance, especially when the malady is only in the incipient stage, since shoddy and other wool substitutes present a similar picture under the microscope, though what is really seen in this case is the broken ends of fibres, and not the separate spindle cells.

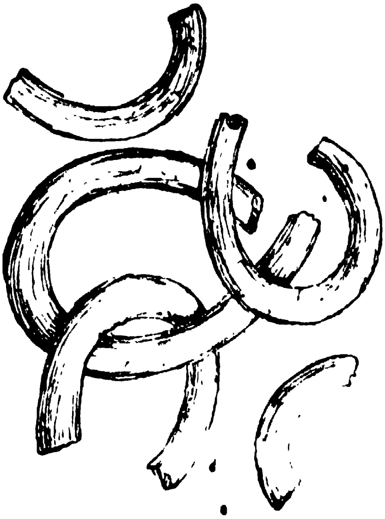

FIG. 12.

The malady in question plays an important and much-dreaded part in the woollen industry, since the affected pieces can neither be properly dyed nor milled, and, besides, the goods are weakened.

An equally characteristic appearance is exhibited under the microscope by wool corroded by alkalis, the wool being curled up in horse-shoe form when the reaction has been very strong (see Fig. 12), or merely turned round in the form of a crosier at the ends when a less powerful reaction has occurred. A similar corrosion of the fibre is often met with after the carbonising process, and, in the subsequent dyeing, gives rise to what is known as "soda-spotting".

Finally, it is also occasionally possible to detect acid corrosion in wool by the aid of the microscope, the fibre being in such case more than usually striated, and in some places, the ends particularly, looks as though hacked to pieces. Unfortunately, the microscopic picture furnished by such wool is not very characteristic, and for this reason the formation of "acid spotting" due to carbonisation cannot always be detected by the microscope test alone, although when the wool has been strongly corroded by acid the microscopic picture is characteristic enough (Fig. 13).

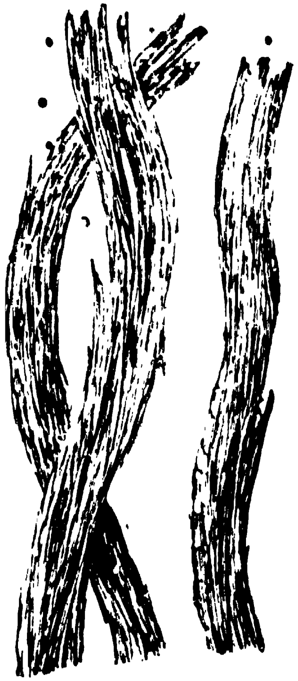

Fig. 13.

Physical Properties.—Wool is a very hygroscopic substance, and can absorb a large proportion of water without becoming appreciably wet. This property is utilised by certain fraudulent dealers, inasmuch as they leave the wool in a damp place, or else sprinkle it with water, in order to increase the weight. For this reason it has become necessary to condition all parcels of wool. The toughest wool generally contains the largest percentage of water, in the case of unwashed wool, the amount of moisture is inversely proportional to the fat content. Although so hygroscopic, wool absorbs moisture in large quantities far less rapidly than the other textile fibres, and therefore requires to be well wetted before dyeing, 1-1½ hours' boiling in water being necessary.

In warm water wool fibre swells up, becomes soft, and, like all horny substances, plastic—*i.e.* retains the shape into which it has been moulded. Several important operations in the finishing process for woollen goods are based on this property of the fibre, as well as on its high elasticity and felting power.

The lustre of wool varies considerably, the straight, smooth wools being mostly superior in this respect to the curly merino wools. Such wools, however, as have a glassy lustre are generally very hard and horny, and are difficult to dye, on which account they must be particularly well wetted.

The colour also varies greatly in the different grades, the best kinds being white, the others yellowish, red, brown, and black. The dark coloured wools are almost impossible to bleach, although not fast to light, and are worked up in their natural shade to dark goods.

Wool greedily adsorbs acids, metallic hydroxides, and dye-stuffs, more especially in the warm. This interesting feature will be fully dealt with in treating of mordanting and dyeing.

Chemical Composition. In the unwashed state wool consists of three parts—fibre, wool fat, and suint or yolk.

The thoroughly cleansed fibre has the same chemical composition as horn and feathers—*viz.* the substance known as keratin, which is classed with the proteids. It consists of carbon, hydrogen, oxygen, nitrogen, and sulphur.

The percentage values obtained for the constituents of keratin by ultimate analysis are worthless, since it is impossible to dry wool thoroughly without decomposition. It is, moreover, almost certain that what we regard as pure wool is not a uniform substance, since if even the purest wool be boiled in water, one or perhaps more organic substances and sulphur pass into solution. The organic matter thus dissolved gives precipitates with silver and lead salts, and is therefore probably of an acid character.

If this boiling be repeated with fresh quantities of water, a point is at length reached when no further extraction occurs.

With regard to the part played by sulphur in the substance of wool, nothing definite is known. A portion of this sulphur can be extracted by solvents, and even, as already stated, by boiling with water, without altering the structure of the wool or its behaviour towards reagents; and it also appears to be in part contained in the soluble matter just referred to. Nevertheless, the whole of the sulphur cannot be extracted without producing structural modifications. These considerations also explain the highly conflicting analytical reports on the percentage of sulphur in wool, the figures ranging from 0·8 to 3·8 per cent.

The presence of sulphur distinguishes animal wools from all other fibres, and may be employed as a means of differentiation between them, a black coloration being produced when wool is boiled with sodium plumbate.

Wool Fat. This, the fatty matter found in wool, is an accidental constituent of wool fibre, but cannot be entirely removed without spoiling the softness of the wool.

Its composition is complex, and has been only partially investigated. It consists of cholesterin and isocholesterin, both in a free state and in combination with oleic acid, stearic acid, hyaenic acid, etc. Free higher fatty acids, and other still unidentified substances, also appear to be present. Wool fat is therefore not a true fat, since it contains no glycerides.

Suint or Yolk. Under this name are comprised all the bodies that are eliminated from raw wool in the washing process, though, scientifically speaking, the term "suint" applies only to the fluid secretion of the skin of the sheep. The amount varies in different wools, and it is an accepted axiom that the larger the proportion of suint the better the quality of the wool.

The extracted and dried suint contains 60 per cent. of organic matters and 40 per cent. of mineral substances. It consists chiefly of the potash salts of oleic acid and stearic acid, probably also of other volatile fatty acids; and, in addition, contains potassium chloride and the phosphates, sulphates, and silicates of calcium, potassium, iron, and magnesium, together with nitrogen in the form of ammonia salts and in the organic compounds.

Both wool fat and suint are recovered from the waste waters of wool-washing establishments, and are utilised in various ways. (See Wool-Washing.)

Behaviour Towards Reagents. In the pure state wool fibre consists of keratin, which is classed with the proteids and has the character of an amido-acid, *i.e.* is both acid and basic. The presence of amido groups in wool has been proved by diazotisation.

Even when stored in the damp, sheep's wool is less subject to mould than vegetable fibres. On being heated in the dry state, wool undergoes slight decomposition, even at 120 to 125 C., attended with liberation of ammonia and slight yellowing; when heated to 140 to 150 C., it also loses part of its sulphur, which is liberated in the form of sulphuretted hydrogen.

The behaviour of wool on combustion and towards water has already been described, and it only remains to state that wool is far more resistent towards water than silk, though unnecessarily prolonged boiling, in damping, mordanting and dyeing, should be avoided, since this turns the wool brown, and lowers its tensile strength. It suffers less when boiled in acidified water, but more when a solution of Glauber salt is used. When heated with water to 200 C., under pressure, complete decomposition and solution occur.

The effect of alkalis on wool has already been mentioned in part. Ammonia in the cold does not attack wool to any appreciable extent, though some loss of substance occurs even when the ammonia is very dilute and the period of exposure brief.

Ammonium carbonate has but very little effect on wool, and is for this reason the best detergent for this material.

Buntrock and Kertesz found that, curiously enough, strong alkaline lyes attack wool less than when more dilute, especially when they contain glycerine. In fact, alkalis of 30 to 40° C. strength, containing glycerine, can be allowed to act on wool for

10 minutes or more, in the cold, and though there is a loss in weight, the wool fibres increase in strength, lustre, and affinity for many dye-stuffs. Treatment with formaldehyde (Kann, Ger. Pat., 141485) enables wool to offer more resistance to the action of alkalis.

Lime acts less powerfully than the caustic alkalis, but extracts sulphur and renders the wool hard and brittle, besides making it more difficult to full. It is for this reason that tanners' wool is such an inferior material.

By the energetic action of barium hydroxide, a substance known as lanugic acid, possessing the general properties of wool, has been isolated from the fibre.

Wool has a greater power of resisting dilute acids than is exhibited by any of the other textile fibres already mentioned, but suffers more or less corrosion when treated with concentrated acids. Thus, if carbonised wool be left for several weeks without neutralising the residual sulphuric acid from the carbonising process, it will be found to have sustained considerable alteration, evidenced by the abnormal loss in weight experienced on boiling it with water. Such wool also behaves in a peculiar manner when dyed, inasmuch as it will then readily absorb methylene green, for example, which is not the case with normal wool.

On the other hand, it has almost entirely lost its affinity for acid dye-stuffs. This observation, which was first made public by the author—in the first edition of the present work—formed the basis of a patent (Fr. Pat., 318711) by the Badische Co., in which wool, by careful treatment with concentrated sulphuric acid, undergoes such a change that it can no longer be dyed with acid dye-stuffs. By weaving this wool with untreated wool, fabrics are obtained which will give two-colour effects in a single dye bath.

A number of methods for the production of crêpe effects are based on the shrinking effect of acids on wool, zinc salts, thio-cyanates or bisulphites being printed on the fabric and steamed.

The adsorptive power of wool for acids is of both theoretical and practical value. For example, if wool be treated in a solution of dilute sulphuric acid, it will take up—in proportion to the concentration of the bath—a larger or smaller amount of acid, which cannot afterwards be completely eliminated by washing with water. Since this adsorption takes place at boiling heat as well, it is not surprising that wool mordanted with sulphates always contains sulphuric acid. Hydrochloric acid is not adsorbed to the same extent; and wool mordanted with tin salt contains little or no hydrochloric acid.

Concentrated nitric acid stains wool yellow, xanthoproteic acid being formed. This property is frequently utilised for producing false yellow selvedges in cloth.

Chlorine or hypochlorous acid has a very powerful effect on wool, the latter absorbing up to 33 per cent. of the reagent, and suffering an entire change of character, being stained brown, losing its felting properties, acquiring a hard feel, and in many cases assuming a silky appearance, inasmuch as it scroops when compressed, and exhibits a greater affinity for dye-stuffs.

However, an entirely favourable modification is produced in wool by the moderated action of hypochlorous acid; and practical use is made of this circumstance—for example, in securing better development of the so-called steam dyes in the printing of woollen piece goods. Of late years, this reaction has also been employed in the production of the so-called "silk wool," a product exhibiting the above-mentioned properties of silk, and obtained by treating wool with an acidified solution of bleaching powder. (Full particulars of the method are given in the directions published by the Badische Anilin- und Sodafabrik.)

Numerous attempts have been made to utilise in practice the changes produced in wool by chloring. If wool, treated in this way, be woven into fabric with normal wool, a crêpe effect can be developed by milling, since the chlored wool has lost its felting properties; and at the same time, a two-colour effect is produced, owing to the increased affinity of the chlored wool for dye-stuffs. Conversely, the affinity of wool for dye-stuffs can be considerably lessened by treatment with alkaline solutions of hypochlorites (Fr. Pat., 318741).

Two-colour effects in all-wool fabrics can also be obtained by precipitating metal tannates on the fibre, and thus greatly lowering its affinity for acid and mordant dyes (Beeke and Beil Ger. Pat., 137947).

Finally, it may be mentioned that true wool hair is dissolved by ammoniacal copper oxide in the warm, whereas body-hairs, and hairs in general, are destroyed but not dissolved by this reagent.

Goat Wool and Camel Wool.

In morphological and chemical character these textile fibres are closely allied to sheep's wool, and the particulars given with regard to that substance apply to them also.

Mohair is the silky hair of the Angora goat, indigenous to Asia Minor; the climate of which country seems favourable to the growth of long silky hair, since the dogs, cats, and rabbits there found are all covered with hair of this kind. Latterly it has been found possible to acclimatise the Angora goat in Cape Colony also.

On account of its stiffness, mohair is used for making plush, and, by reason of its handsome lustre, it is also employed in fine fabrics, for decorating cloth, and for fancy yarns in place of silk.

Under the microscope, mohair is distinguishable by remarkably broad and regularly distributed striations, the scales are thin and serrated.

Cashmere, or Thibet wool, is the soft down of the Cashmere goat (*Capra hircus laniger*), indigenous to Thibet. It forms the material for the justly renowned Indian shawls, and, on account of its great softness, is also used in the European woollen industry, mainly for producing a nap on winter clothing.

It is worthy of remark that this wool is more difficult to dye than that of the sheep.

Alpaca, Vicuna, and Llama. These fibres are furnished by camel-goats, of the Auchenia family, inhabiting the mountains of Peru and Chili. They are mostly of a red-brown to black colour, but are of only minor importance to the European textile industry.

It should be noted that the commercial product known as vicuna or vigogne is not obtained from the vicuna, but is a mixture of wool and cotton; further, that an artificial wool, or wool substitute, is met with in commerce under the name of alpaca.

These exotic wools are frequently infested with a micro-organism (*Bacillus anthracis*), which produces the disease known as anthrax (wool-sorter's disease) in man, and engenders a species of typhus in cattle and horses. Consequently, the rooms where these wools are sorted should be well ventilated, and the sorters should wear respirators.

Camel Wool. On account of its strength and softness, camel wool has latterly been largely used for making bedcovers and winter clothing. As it cannot be bleached, it is used either in the natural colour, or dyed dark brown or black.

Cow Hair.—This fibre being cheap, and possessing a certain—though not considerable—amount of felting power, is now somewhat largely used in the manufacture of coarse blankets and bedcovers.

Wool Substitutes.

The first experiments on converting woollen rags into fibre suitable for spinning were made in England in 1845, the product being put on the market under the name of shoddy. This industry has increased to a very considerable extent, and, according to an old estimate made by Grothe, about 33 per cent. of the total wool manufactured consists of wool substitutes; in fact, of all the samples of woollens examined by him, only 15 per cent. were free from such admixture. At the present time, the quantity of wool substitutes manufactured and used is far greater. Shoddy factories now exist in nearly every country in Europe, and it is therefore natural that all cheap woollen goods should contain wool substitutes; in fact, many low-priced cloths consist of 70 per cent., and more, of such materials. On the other hand, they can only be used for the under wefts of worsted fabrics.

There are several varieties of wool substitutes, the value of which stands in direct relation to the quality of the waste from which they are produced. The chief members of the series are the following:—

Shoddy.—This is made of waste or rags from pure unmilled woollens, flannels, bedcovers, curtains, and also from knitted and twisted goods. The resulting fibres are about an inch long, and are sorted according to colour and fineness, vegetable fibres being eliminated by carbonising.

Mungo is obtained from milled woollen rags, and being of much shorter staple than shoddy (¼-½ inch) is therefore of less value than the latter.

Alpaca, or extract wool, is a long staple substitute from fine unmilled cloth waste, and generally contains a good deal of vegetable fibre. The crux of the process, therefore, resides in the operation of carbonising.

Thibet Wool substitute is recovered from light cloth waste.

Cosmos Fibre. This contains no sheep's wool at all, being made of waste from flax, jute, and hemp fabrics; it also frequently contains fragments of hopbine, nettle fibre, etc. Belgium and North America are the sole centres of production.

In addition to the foregoing adjuncts, use is made in the woollen industry of the short fibre obtained as a waste product in the shearing or cropping of cloth. This material is milled in, to the extent of about 20 per cent., on the under side of cloth, the operation being known as "impregnating". It can be detected under the microscope by the shortness of the fibres and by their truncated ends.

Testing Wool Substitutes.—In most cases all that is requisite is to determine the amount of cotton present, but in a complete analysis the percentage of water and fat (the latter being usually added to facilitate spinning) must also be determined, and a qualitative test made for silk.

It is very important to get a large representative sample, which should be well mixed together, before being divided up for the various tests.

Water is ascertained by drying a 5 to 10 grm. sample at a little over 100° C.

The fat is estimated by extracting a dried sample with petroleum ether.

The percentage of cotton is found by digesting a fat-free sample—of at least 10 grms.—for a quarter of an hour at boiling temperature in 8° B. caustic soda. This dissolves out the wool, leaving the cotton behind for weighing after filtration through a linen cloth, washing out all the alkali with boiling water, and drying.

Silk, which is occasionally present, need only be tested for qualitatively. This should never be omitted, since, unlike cotton, silk is not removed by carbonising, but remains behind in the wool, and will, by reason of its different affinity for dye-stuffs, cause irregularities in dyeing. The test is performed as follows: A sample of the substance is dyed with logwood, which stains only the wool, leaving the cotton and silk almost unaffected and easily recognised by their lighter shade. A sample is then examined for silk under the microscope. Acid dye-stuffs (such as acid black ST, in a strong acetic bath) are also used.

Examining Fabrics for the Presence of Wool Substitutes.

With this object, a few fibres are cut from the fabric by the aid of a sharp knife and placed under the microscope, whereupon the wool substitutes will be recognisable by their shape and colour. That the form of these fibres will be different from ordinary wool can be readily understood when it is remembered that, in addition to the tearing process they have to undergo (in the case of shoddy and mungo, at least), the wool substitutes have been through the finishing process twice over. Hence these fibres exhibit ragged ends, owing to the loss of the scales, and they are frequently also partly broken in the middle. As, however, wool hairs attacked by mould also exhibit a similar appearance, care is necessary to prevent confusion.

Variety of colour is the best indication of the presence of artificial wool, since, although the different colours are sorted out in the making, this cannot be done with perfect accuracy, and therefore the fibres of wool substitutes are usually many-coloured, unless, which rarely happens, the material is all white. Thus, in examining a red cloth, for example, if it be found to contain blue and green fibres as well, the presence of wool substitutes may be justifiably assumed. In the case of very dark coloured materials the colour should be first partly removed by boiling with a weak alkali or dilute acid before making the examination.

Of course, in the case of coloured mixture fabrics, hairs of more than one colour (usually two or three) may be expected. To prevent deception it is also advisable to examine the colour of the selvedge; blue cloths, for instance, generally have a yellow selvedge, and it may happen that a few hairs almost invisible to the naked eye—from this selvedge will come on to the cloth, which will then seem to contain yellow fibres in the microscope sample. In any event, the examination should not be confined to a single sample.

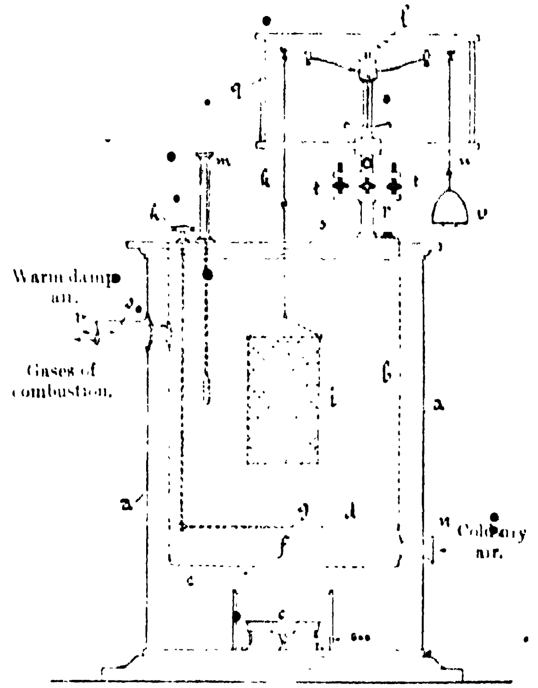

FIG. 14.

Sometimes the presence of wool substitutes can be indirectly determined by a qualitative examination of the ash left by the material on combustion. Thus, if the sample have been dyed with a Ponceau dye, and chrome be found in the ash, the presence of artificial wool is indicated, since these dyes are never fixed with chrome salts, and therefore the latter must have been introduced in a wool substitute.

Conditioning.—As already stated, silk, being an expensive and also hygroscopic substance, has to have its actual weight determined when sold. This operation is performed in official institutions, known as "conditioning houses," the *modus operandi* being as follows:

The parcel of silk is first weighed, after which samples are drawn, to the extent of about 1500 grms., from different parts of the whole. The sample is divided into three parts, two of them being weighed to ½ grm. and then placed in the apparatus shown in Fig. 14, where they are dried, until of constant weight, by a current of air heated to 110 C. If the resulting weights agree to within ½ per cent., the average is taken, but when a greater difference exists the third part of the sample is dried in the same way, and the mean of the three determinations is adopted. The standard commercial weight is found by adding 11 per cent. to the dry weight. In the case of mixed yarns of silk and wool the standard of permissible moisture is 16 per cent. of the dry weight of the material.

Conditioning houses of this kind exist in London, Paris, Lyons, Vienna, Crefeld, Zurich, Basle, Turin, Milan, Verviers, etc.

Latterly the custom has arisen of conditioning both wool and cotton as well as silk, the work being done in just the same manner. The officially permitted percentages of moisture are as follows :-

For worsted and worsted yarn	18¼ per cent
For unwashed wool, woollen waste, combings, and carded yarn	17 „
For cotton and cotton yarns .	8½ „
For artificial silk	11

CHAPTER II.

WASHING, BLEACHING, AND CARBONISING.

Washing and Bleaching.

BROADLY considered, any operation performed with the object of cleansing a textile fibre at any stage of manufacture or improvement may be included in this category; but, in their more restricted sense, washing and bleaching are terms confined to the cleansing of the textile fibres in their crude state in order to prepare them for the subsequent operations of dyeing, dressing, &c. Thus, in speaking of wool-washing, the first process of purification to which the wool is subjected before spinning is meant, and not the rinsing of dyed wool, for example.

Corresponding operations are not always described by the same names in different branches of the textile industry, and, conversely, the same term is differently applied. Thus the term "cotton bleaching" comprises the entire set of operations employed to free the cellulose from all natural and other impurities, whereas, in the case of silk and wool, the term "bleaching" implies only the more restricted sense of the word, being confined to the operations effecting the actual decoloration of the fibre. Again, the first cleansing process applied to raw silk is not called "washing," as in the case of wool, but is termed "scouring," or "removing the bast".

The means or reagents employed for cleansing the fibres also differ considerably, according to the nature of the fibres in question, the stage of manufacture, and the nature of the impurities to be removed. For instance, one would not attempt to cleanse animal fibres with caustic alkalis, and raw fibre must be cleansed in a different manner to that employed for the same fibre when dyed. Thus, raw silk is freed from sericin by washing with soap and soda, whereas dyed silk is merely rinsed with water alone, if at all.

Raw wool is also washed with soap and soda; the same materials are likewise used, though in a different way, to free the yarn from the oil applied in the spinning process, whilst the dyed pieces are merely rinsed with water or cleansed with soap or fuller's earth. Raw cotton is freed from natural impurities by energetic treatment with caustic alkalis, soda, alkaline earths, etc., sometimes also with acids to remove size. When dyed, however, it is mostly washed with water alone, whilst printed goods are treated with soap, malt, etc.

The present chapter deals solely with the purification of the raw fibres in their undyed state, the various washings subsequent to dyeing and printing being postponed to a more suitable part of the book.

The reagents employed may be divided into two classes, detergents and bleaching agents the former comprising water, soda lye, ammonia, sodium carbonate, ammonium carbonate, quicklime, magnesia, hydrochloric acid, sulphuric acid, soap, resin lyes, benzine, oil of turpentine, etc.

The author takes it for granted that the reader is acquainted with the properties and examination of these materials, and will therefore confine himself to dealing with water, and that, too, merely from a textile point of view.

Water plays an important part, not only in washing and bleaching, but also in the operations of dyeing and printing fabrics. Of the various substances that may be present in water, the following alone are of interest to us, *viz.*:

1. Solid matters in suspension.
2. Salts of lime and magnesia, which produce "hardness".
3. Other less common impurities, such as iron, humus acids, alkali carbonates, and sulphuretted hydrogen.

Turbid water containing matters in suspension must be clarified before use, by filtration or settling. Another method of clarifying impure water is to boil it with bran and skim off the frothy scum.

Wood shavings form a very good filter for impure water. Pale and bright dyeings can only be obtained when perfectly clear water is used, because, when dyed in water that is at all cloudy, the fabric will act as a filter and absorb the suspended impurities.

From the washer's and dyer's point of view, the most important defect in water is hardness, since hard water is unsuitable for either washing or dyeing. If such water be used for, say, washing textile fibres, the lime and magnesia present will be thrown down as insoluble soaps of these metals, and thus, not only is there a considerable waste of soap, but the precipitated compounds adhere to the fibre and are liable to cause spotting. Therefore, to render hard water fit for use, it must first be purified, by one or other of the numerous known technical methods. In some cases it is sufficient to treat the water with soda, which throws down a large proportion of the alkaline earths. A more economical plan, however, especially when the water is to be used for scouring silk, is to first throw down the bicarbonates of lime and magnesia by simple boiling, and then add the soda. In this manner a saving of soda is effected and the water is more effectually softened than by the first named method.

For dyeing, only the so-called temporary hardness of water produced by the bicarbonates of lime and magnesia is injurious, except where the dyeing of silk in a bast soap bath is in question, in which event the soap may also precipitate the lime and magnesia compounds, producing permanent hardness.

Temporary hardness may cause the precipitation of basic dye-stuffs and mordant dyes, the colour base being thrown down in the first case, and the lime or magnesia salt of the dye-stuff in the other; *i.e.* with basic dyes the alkaline earth carbonates act by the alkaline reaction they impart to the dye bath, and in the other case by the formation of insoluble salts. In either event the use of hard water is attended with a loss of dye; this is specially noticeable in the case of dyeing with logwood and various alizarine dyes. In the case of basic dye-stuffs, the colour bases precipitated in a resinous condition are liable to spot the fabric permanently.

Hardness in the water does not matter when acid dyes are used, or in mordanting wool, since in these cases acid baths are used; only when mordanting with cream of tartar does the water require to be corrected beforehand, since otherwise a portion of the tartar would be precipitated as calcium tartrate and lost. No harm is caused by hard water in mordanting cotton and silk; in fact, hard water is preferable to soft for fixing the mordant on silk.

In order to fit hard water for dyeing, it is "corrected" by neutralising the contained carbonates with an acid, the amount required being ascertained by titrating a small sample—about 2 litres in a porcelain basin, with decinormal hydrochloric acid, using methyl orange as indicator. In practice, the acids used are acetic acid or sulphuric acid; oxalic acid cannot be recommended, since, though it precipitates all the salts of lime and magnesia in an almost complete manner, the pulverulent oxalates are liable to be deposited on the fibre, and are then difficult to wash off.

It should be an invariable rule to use none but corrected water for dyeing, though when an acid dye bath is employed the correction of the water is effected at the same time as the acidification of the bath.

When the water has been corrected no precipitation of the dye-stuff will ensue from the alkaline earths, these being now in the state of acetates or sulphates, of a more strongly acid character than the mordant dye-stuffs themselves.

Water containing iron[1] or sulphuretted hydrogen cannot be used for dyeing except under special circumstances; and ferruginous water is altogether unsuitable for bleaching. Water of this kind has a deadening effect on many bright colours, such as alizarine red, cochineal scarlet, etc.

Water containing sulphuretted hydrogen may exert an injurious influence when used in mordanting with metallic oxides which give insoluble coloured sulphides.

Water exhibiting an acid or alkaline reaction, from the presence of humus acids or alkaline carbonates respectively, can be fitted for use by careful neutralisation.

Purifying Waste Water from Dyeing and Bleaching Works.—This is too wide a subject to be exhaustively dealt with here, though a brief mention cannot be omitted. The best method to adopt in dyeworks is to run all the various bath liquors into a large collecting tank. Here the different mordants and dyes precipitate each other, the reaction being completed by an addition of lime. Ferrous sulphate, lime and magnesium chloride, and a mixture of ground lignite and aluminium sulphate (Rothe-Degener) have been found suitable for purifying these effluents.

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[1] The Linde and Hess process for eliminating iron from water has proved satisfactory.

For decolorising purposes, an addition of aluminium hypochlorite—a clarified mixture of alum and bleaching powder—is advisable, any excess of this reagent being rendered innocuous by adding ferrous sulphate.

Bleaching Agents.

By the term bleaching we understand destruction of colour, in the present case the natural yellow-brown colour of the textile fibres in their crude state.

The requirements exacted of bleaching agents in practice are threefold: (1) they must really bleach, *i.e.* convert the yellow colour of the crude fibre into a pure white; (2) they must not corrode the fibre; and (3) they must be cheap.

Only two chief bleaching agents are known, and these at the same time may serve to represent the two groups into which these agents are divided: the first is oxygen, the other sulphurous acid. In the former case the bleaching effect is the result of a destruction of the colouring matter by oxidation; but in the second group the process cannot be expressed by a single word, and, moreover, has not yet been fully elucidated. However, to distinguish these bleaching agents from the others, they may be termed reducing agents.

Mention may also be made of certain substances which, though not used as actual bleaching agents, act as discharges on dyed fabrics. They, too, destroy colour; and it is impossible to draw a hard and fast line between them and bleaching agents.

Finally, there are various other substances which impart a bluish-white tinge to textile fibres; these, however, are not bleaching agents but colorants, their action being to mask the natural yellow colour of the fibre. Their description will therefore be postponed.

(*a*) **The Oxidising Bleaching Agents.**—This class includes oxygen itself, ozone, chlorine, bromine, hypochlorites, peroxides, chromic acid in the form of potassium bichromate, permanganic acid as potassium permanganate, and potassium ferricyanide. Whichever of these substances be employed, their action is invariably attributable to nascent oxygen.

Chlorine acts only in the presence of water, perfectly dry chlorine having no bleaching action. The reaction is based on the decomposition of water and liberation of oxygen—

$$Cl_2 + H_2O = 2HCl + O.$$

Bromine acts in a similar manner.

The hypochlorites act by the decomposition of the liberated hypochlorous acid into hydrochloric acid and oxygen

$$HClO = HCl + O,$$

whence it follows that the activity of these salts can be increased by an acid setting the hypochlorous acid at liberty.

The peroxides, and also potassium bichromate and potassium permanganate, when brought into contact with readily oxidisable bodies, undergo decomposition and liberate oxygen, which then acts as a bleach

$$H_2O_2 = H_2O + O;\ BaO_2 = BaO + O, \text{etc.}$$
$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + O_3.$$
$$K_2Mn_2O_8 = K_2O + 2MnO + 5O.$$

All these bleaching agents act more energetically than oxygen itself, because the oxygen they liberate is in the nascent state. In all cases the presence of water or moisture is indispensable for the performance of the bleaching reaction, perfectly dry oxygen having no oxidising power.

Textile fabrics intended for bleaching must first be suitably cleansed; otherwise a large proportion of the bleaching agent will be consumed in destroying the impurities which can be got rid of more effectually and cheaply by the use of soap.

Atmospheric Oxygen and Ozone.—The oxygen of the air is the oldest bleaching agent known, and is the active ingredient in the process of grass bleaching, which was formerly employed for cotton and linen, but is now almost entirely confined to the latter class of goods. Whether in this process the oxygen acts partly in the condition of ozone has not been definitely ascertained.

The decolorising or discharging of dyed colours is also nothing else than a process of oxygen bleaching.

In recent patented processes by Siemens and Halske, atmospheric oxygen is ozonised by an electric current, and in this form is used for bleaching fibres, principally linen. The operation is performed in a closed illuminated glass chamber, and is claimed to occupy only one-third the time consumed in the ordinary grass bleach.

Some oils possess the property of absorbing atmospheric oxygen and, under the influence of light, converting it into ozone. Oil of turpentine is one of these, and, in addition, exercises a cleansing effect on textiles, especially in presence of water and an alkali; in fact, a mixture of ozonised turpentine and alkali has been recommended as a bleaching agent by Depierre and Georgievics.

Chlorine was formerly used for bleaching cotton, but the method never attained any practical importance. Latterly, this reagent has again been advocated by several, Breinl and Karrer having recommended it for bleaching cotton on the bobbin, and Leykham of Josefsthal for jute. The Brin's Oxygen Company employs a mixture of chlorine and oxygen for bleaching. Finally, it may be mentioned that proposals have been made to intensify the bleaching action of chlorine by the influence of the electric current as applied to oxygen by the Siemens and Halske method.

Bromine has been recommended for bleaching Tussah silk, the excess of reagent being afterwards removed by the aid of a sulphite, which, in turn, is eliminated by an acid bath.

Bleaching powder, or "chloride of lime," is one of the oldest and most important of the bleaching agents. According to Ditz, it consists of a variable mixture of $Ca\begin{matrix}Cl\\OCl\end{matrix}.H_2O$ and $Ca\begin{matrix}OCl\\Cl\end{matrix}.H_2O$.

Bleaching powder is the main bleaching agent used for all the vegetable textile fibres except jute; but, like chlorine or other hypochlorites, is unsuitable for animal fibres. It must be stored in well-closed vessels, in a cool place, since otherwise it undergoes rapid decomposition.

Particular care is necessary in dissolving this reagent in water, it being essential to avoid heat, or decomposition will ensue. The solution should be perfectly clear and free from particles in suspension, since these would be deposited on the fibre to be bleached and produce "super oxidation," *i.e.* not only destroy the colouring matter of the fibre, but convert the cellulose into oxycellulose. As the latter has a greater affinity than the former for dye-stuffs, the result would be to form dark spots impossible to eliminate. In cotton-printing these oxycellulose spots turn brown when steamed, and the fibre exhibits more or less corrosion. If bleaching powder be treated with too much water at first it forms lumps that cannot be afterwards reduced. Consequently the powder, after being passed through a crushing mill, is first carefully mixed to a paste with a small quantity of water, and then treated with enough water to form the solution. It is advisable to use two stone tanks for this operation, the solution being prepared in the one and poured, when clear, into the second, where it is reduced to the proper strength. The common practice of recording the strength of bleaching powder solutions in degrees of the Beaumé hydrometer is irrational, since whilst the useless substances present, such as calcium hydroxide, calcium chloride, etc., increase the density of the solution, the active free chlorine has the contrary effect. Hence the density is no criterion at all of the real strength of the solution. In fact, this can only be ascertained by chemical means, *e.g.* titration with potassium iodide, sodium hyposulphite, and starch paste, or with arsenious acid (Penot's solution). The proper strength of solution to use for bleaching depends mainly on the nature of the fibres under treatment, their capacity for resisting the action of bleaching powder varying. Cotton is the least susceptible of all; nevertheless care is required even in this case. The "chemicking," as the bleaching with chloride of lime is called, is the most risky operation of the whole bleaching process, because here the corrosion of the fibre is most likely to occur. In practice the strength of solution used varies from 0·2 to 2½ B.

When a fibrous material, impregnated with dissolved bleaching powder, is exposed to the air, the bleaching effect is increased in comparison with the action produced when the same is merely left immersed in the liquid, the reason for this being that the hypochlorous acid is liberated by the carbon dioxide in the air. Fabrics impregnated with such a solution must not be exposed to direct sunlight, or the oxidising action of the bleach will be so strong as to corrode the fibre and reduce its strength.

This method of immersion and exposure, however, is only practised in the case of some fabrics which are to be sold in the undyed state, the usual method being to steep the fabric for several hours in a weak solution of bleaching powder.

Moreover, it must be remembered that simple washing with water is insufficient to entirely remove the bleaching powder solution from the fibre and consequently the material must be afterwards soured in an acid bath, or, in the case of household linens, treated with an "antichlor," since otherwise the fibre will be more or less weakened in course of time.

Finally, bleaching powder can be used in the manufacture of other hypochlorites, aluminium hypochlorite, for example, being prepared by treating bleaching powder solution with alum.

Sodium Hypochlorite. This compound is prepared for bleaching purposes by acting on bleaching powder with sodium carbonate.

This salt is gentler in its action than the lime compound, probably because the latter—owing to the less ready solubility of calcium carbonate—is more easily decomposed by atmospheric carbon dioxide, and the liberated hypochlorous acid comes into action more energetically than in the case of sodium hypochlorite. For this reason no weakening of the fibre occurs in bleaching with the sodium salt, though almost inevitable when bleaching powder is used. Other advantages of the former are that it does not harden the fibre, and that the acid bath, after bleaching, is dispensed with, the reagent being easily removed by a simple rinsing in water.

Again, the bleaching process goes on better by simple immersion in the sodium hypochlorite solution than in the usual method practised when bleaching powder is used. Not only does sodium hypochlorite form the most important bleaching agent for jute, but its use for cottons has grown more and more in favour of late—an extension that may be expected to continue to the entire suppression of bleaching powder, owing to the ease with which the sodium salt can be prepared by electrolytic methods, the product being cheaper (provided motive power be available at a reasonable cost) and always obtainable of constant strength.

The various forms of electrolytic apparatus used in the production of sodium hypochlorite differ from each other in details of construction alone, the method of working being practically the same in all. A 7 to 16 per cent. solution of common salt is employed, which is kept at a temperature of 21° to 23° C. during the electrolytic process. For this purpose the solution is circulated by means of a pump, which transports the liquid from the electrolyser into a cooling tank and back again. This operation is repeated until the solution has attained the desired percentage of active chlorine. In most cases the electrolyser is divided up into cells, so that the liquid has to take a devious course. Kellner uses platinum-iridium electrodes; Schoop, platinum-iridium and carbon; Rass and Oettel, electrodes of material resembling carbon.

Ammonium hypochlorite has been proposed for bleaching Tussah silk; and aluminium hypochlorite and magnesium hypochlorite have also been recommended as bleaching agents.

Hydrogen Peroxide is the best bleaching agent, and can be recommended for all kinds of fibre, as well as for removing stains, and for bleaching the hair. It possesses the great advantage over all its competitors, that it does not attack the fibre in any way; but it is too expensive for general use. Up to the present its chief application has been in the bleaching of wool, and here it exhibits the decided advantage of producing permanent decoloration, which was hitherto unattainable by the use of sulphur. Nevertheless, hydrogen peroxide alone is incapable of furnishing a perfectly pure white.

Hydrogen peroxide is met with in commerce as an aqueous solution, containing 1·5 per cent. of active oxygen, the solution being of 12 per cent. (vol.) strength. It is rather unstable, and must therefore be stored in the dark; an addition of glycerine, however, is said to increase its stability. The strength of the solution is ascertained by titration with potassium permanganate, or with potassium iodide and sodium hypochlorite. It should be as pure as possible, since impurities like alumina, baryta, magnesia, etc., may exert a catalytic decomposing action. For this reason it cannot be stored in metallic vessels, though the heating coils may be of lead. Iron nails in the bleaching vessel, as also atmospheric dust, exert a catalysing influence on hydrogen peroxide. For this reason, the bleaching vessels must be covered up, and they must also be bleached out, when new, before use. In draining goods containing hydrogen peroxide, the hydro-extractors must be lined with a cloth, to prevent direct contact with the metal. From what has already been said, it will be self-evident that even the water used for diluting the hydrogen peroxide must be pure.

Alkaline solutions of this reagent are particularly unstable, and consequently these alone are employed in bleaching, the oxidising action being otherwise too slow. The *modus operandi* is as follows. The commercial solution of peroxide is diluted with two to ten volumes of water, and, before use, receives an addition of 20 grms. of ammonia per litre (of peroxide). The strength depends on the nature of the material under treatment, the concentration being the greater in proportion as the latter is the more difficult to bleach.

The bleaching effect produced by hydrogen peroxide also depends to a considerable extent on the alkali used. Sodium silicate (water glass) has been found superior to ammonia, because it allows the bath to be heated to a high temperature. In such a solution the material to be bleached is usually treated in the warm for 1 to 2 hours. The suggestion of Prud'homme and Koechlin to add magnesia, instead of ammonia, to the bleaching bath, has not answered in practice. The material to be bleached is either left in the liquid for about ten hours, or is merely impregnated therewith, the excess being wrung out, and the stuff left exposed to the air for some time. This treatment is repeated as often as necessary, care being taken to exclude dust. More uniform bleaching, however, is obtained by leaving the material in the bleacher.

The following method has of late been largely used for bleaching woollens, especially for mousselines that are to be afterwards printed: The suitably cleaned goods are entered, full width, in a bath of hydrogen peroxide (diluted with two to ten parts of water, and containing an addition of ammonia), after leaving which they are rolled on a wooden roller and left for twenty-four hours, covered up with damp nettles. The fabric is next washed, passed through a bath of 35° B. (diluted with two to ten times its volume of water, according to requirements, as determined by experiment for each class of material), then rolled up and left as long as before. On unrolling the fabric, it is dried, passed through a weak acid bath (1° B. hydrochloric acid), and finally washed. This method furnishes an excellent white.

Sulphuring in a sulphur chamber may be practised instead of the bisulphite method. This after-treatment both gives a better white and also improves the feel of the goods.

Processes for bleaching vegetable fibres with hydrogen peroxide have frequently been brought forward (*e.g.* by H. Koechlin), but, up to the present, they have, for economic reasons, not been adopted.

Sodium Peroxide. This new bleaching agent is manufactured by the Aluminium Company, Ltd., London, etc., and is prepared by passing air freed from carbon dioxide at a temperature of 300° C. over metallic sodium contained in aluminium vessels.

The commercial product contains about thirteen times as much ctive oxygen as hydrogen peroxide, and is only recommended or bleaching animal fibres. Some precaution is necessary in its application, since it hisses and disengages considerable heat when dissolved in water; and if brought suddenly into contact with a large quantity of that liquid is liable to produce an explosion. The storage receptacles must therefore be kept tightly closed and in a dry room.

The bleaching vessel is first charged with the requisite quantity of water, which should be as cold as possible, and with sufficient sulphuric acid to neutralise the peroxide (the amount of which has been previously ascertained by a preliminary trial with materials of the same kind as those to be bleached). The peroxide is added by degrees and stirred in. The reaction of the bath is tested with litmus paper, and should be neutral, or only faintly alkaline, a little ammonia or water glass being added if the liquor is acid. The goods to be bleached are then entered, and the bath is slowly heated to a temperature not exceeding 80° C. (176° F.), lower being advisable. The goods are left in the bath for 2 to 4 hours, then treated with water strongly acidified with sulphuric acid, and afterwards thoroughly washed and dried.

Barium Peroxide serves for bleaching Tussah silk, and was also recommended by Mullerus for bleaching cotton. In using this substance, however, the fact that it contains barium hydroxide—a strong alkali capable of corroding animal fibres—must not be forgotten; and it should therefore be washed with water before use. The commercial product contains 8 per cent. of active oxygen.

Potassium Permanganate. This substance is a very powerful oxidising agent, and is frequently used for this purpose in the laboratory. It must be kept in closed vessels, away from the light, and its solutions are readily decomposed.

Bleachers make use of this salt for treating wool, jute, straw, leather, etc., the mode of application being as follows. The material to be bleached is first treated with a dilute solution of lukewarm permanganate, until the colour turns to brown (formation of potassium manganate). In bleaching animal fibres this solution receives an addition of magnesium sulphate, which, by forming magnesium hydroxide (insoluble) and potassium sulphate, prevents the corrosion of the fibre otherwise resulting from the formation of caustic potash. To remove the brown coloration the material is next treated with a cold dilute solution of bisulphite, or a similar solution of sulphurous acid and borax (prepared by saturating dissolved borax with sulphur dioxide), and finally washing in slightly acid water, followed by pure water.

Owing to its cheapness this method is largely used for woollens, but far less frequently than the sulphur process described below. The permanganate method is very serviceable where stained woollen goods are to be treated with a view to render them fit for sale, if only as inferior goods. It is also useful in bleaching jute, and is actually employed for that purpose.

Potassium Bichromate, in conjunction with sulphuric acid, has a very powerful oxidising effect, and is used for bleaching oils, straw, etc., though not for textile fibres. It has been recommended for jute, but is unsuitable, as it attacks the fibre.

Owing to its property of destroying the colour of indigo, it is used as a discharge in blue printing (*q.v.*).

Potassium Ferricyanide has been proposed by Kassner as a bleach for textiles, and, as a matter of fact, its bleaching action is very powerful in alkaline solutions, potassium ferrocyanide being formed. Nevertheless, the only use made of this property at present is in discharging indigo.

(*b*) **The Reducing Bleaching Agents.** This class comprises free sulphurous acid, bisulphite, and hydrosulphurous acid.

The bleaching action of these substances is not yet fully elucidated, but is assumed to consist in a reduction of the pigmentary matter to its leuco compound, and in the combination of this latter to form a colourless substance. This hypothesis is apparently favoured by the fact that animal substances bleached with sulphurous acid have a tendency to revert to a yellow shade, especially after being treated with alkalis, thus showing that the colour was not really destroyed in the first place, but converted into a colourless compound, which in time has become decomposed and allowed the original colour to reappear.

This phenomenon is most clearly shown in the case of goods that have been bleached with free sulphurous acid. In addition to animal fibres, jute is often bleached by this class of reagent.

Sulphurous Acid is used either in the gaseous form or as an aqueous solution of bisulphite, the former being the one most in use. Aqueous solutions of the gas are the least adapted for bleaching, being always contaminated with sulphuric acid.

Wool and silk are generally bleached with gaseous sulphurous acid in so-called "sulphur chambers," which are spacious brickwork chambers, fitted with peep-holes for inspecting the goods, the latter being hung on supports inside. The sulphur is placed in iron pots, or in sunken brick pans, which can be fed from the outside. To begin bleaching, the sulphur is ignited, the doors, etc., are closed, and the goods left exposed to the sulphurous fumes.

The quantity of sulphur used must bear a certain proportion to the size of the chamber, in order that a sufficient supply of oxygen for the combustion of the sulphur may be available. The volume of oxygen at disposal for this purpose can be readily calculated from the cubical capacity of the chamber, and a considerable margin in excess of the actual requirements must be allowed for in practice. Should the oxygen be insufficient for complete combustion, the sulphur ceases to burn and sublimation readily ensues, with the result that the goods get stained with yellow patches that cannot be afterwards eliminated. To prevent this evil the sulphur pans should be covered with a sheet of lead, or with felt laid over a wooden grid.

The average consumption of sulphur required to bleach woollens is 6 to 8 per cent., or for silk 5 per cent., of the weight of material treated. The operation generally takes six to eight hours, but must be repeated three or four times, according to requirements.

To prevent condensation and the consequent spotting of the goods by droppings, a number of heating-plates or steam-pipes are arranged under the ceiling of the chamber, and a chimney with a good draught is provided for carrying off the sulphur fumes after the bleaching is finished.

The sulphur chamber should be entirely free from iron fittings, since the sulphur trioxide invariably produced when sulphur is burned unites with the moisture present, thus forming sulphuric acid, which would rust the iron.

Like all other bleaching agents, sulphurous acid requires the presence of water in order that the reaction may occur at all; consequently the goods must be introduced in a damp state into the chamber.

Light goods, especially those for printing, are bleached by the continuous process, the apparatus used being of the same type as the first steamer employed in calico-printing. In large works two sets of apparatus are mounted side by side; the goods are entered damp and are carried onward over rollers fitted with hardened lead pins. The passage through the chamber occupies ten minutes; and light goods are put through twice, heavy articles three times.

In addition to the more serious defect of the sulphur bleaching process, *viz.* yellowing, it is also attended with the following disadvantages: the sulphuric acid, always formed, retards the bleaching action of the suphurous acid, and may also be a source of danger to cotton in mixed fabrics; and the process makes the wool harsh, though this can be remedied by a treatment with warm soap and water afterwards. Nevertheless, owing to its cheapness and the beautiful white it produces, the sulphur method is still the one most largely used in bleaching animal fibres.

Sodium Bisulphite ($NaHSO_3$) is more generally used for bleaching on a small scale, and especially in preparing goods for dyeing light shades or for printing (woollens). There are two methods of procedure in the case of yarns: either the goods are immersed in a solution of the bisulphite and hydrochloric acid, or else they are treated with the bisulphite first and the acid after. The first is the one most practised, and, as a matter of fact, is equivalent to bleaching with an aqueous solution of sulphurous acid. The goods are left to soak for several hours in a weak solution of bisulphite, containing a corresponding quantity of hydrochloric acid, and are then washed, the process being repeated if necessary. When the bisulphite and acid are used separately, the goods are steeped for some time, *e.g.* overnight, in a fairly strong (about 20° B.) solution of bisulphite, after which they are passed through very dilute hydrochloric acid, and are finally washed with water.

In bleaching woollen piece goods for printing, they are first washed with soda and soap, then padded on the jigger with a solution of 1 part by weight of bisulphite (35° B.) and about

3 parts of water; after which they are left, rolled up, for one to two days and soured.

Hydrosulphite. Hydrosulphurous acid, a reduction product of sulphurous acid, was recognised, by its discoverer, Schutzenberger, as an excellent reducing agent, and was recommended by him for rendering indigo soluble in vat dyeing. The sodium salt is obtained by the action of zinc on sodium bisulphite, according to the equation

$$4NaHSO_3 + Zn = \underbrace{Na_2S_2O_4}_{\text{Sodium hydrosulphite.}} + Na_2SO_3 + ZnSO_3 + 2H_2O$$

The following recipe for its preparation is given by the Badische Anilin & Sodafabrik. 130 grms. of zinc dust, previously made into a paste with about 70 c.c. of water, are slowly added to 1 litre of bisulphite (38 to 40° B.), and stirred in, along with cold water or ice. The operation is best performed in a wooden vessel fitted with mechanical stirrers. After agitation for twenty minutes longer, the solution is left to stand for an hour, whereupon 600 c.c. of milk of lime (20 per cent. strength) are slowly stirred in. After standing for two hours, the clear solution is drawn off from the sediment and stored in casks. If kept in closed vessels, this solution will remain for several weeks without any appreciable decomposition.

In the above method of preparation however, the process is imperfect, as can be seen from the equation. A better yield is obtained by adding sulphurous acid, $2NaHSO_3 + Zn + SO_2 = Na_2S_2O_4 + ZnSO_3 + H_2O$.

Sodium hydrosulphite is an unstable compound, which will keep for but a short time in solution, and then only if out of contact with air. It decomposes in accordance with the equations—

$$2Na_2S_2O_4 + H_2O = Na_2S_2O_3 + 2NaHSO_3;$$
$$Na_2S_2O_4 + 2NaHSO_3 = 2Na_2SO_3 + H_2S_2O_4.$$

Free hydrosulphurous acid is still more unstable.

Bernthsen, who ascertained $Na_2S_2O_4$ to be the formula of sodium hydrosulphite, was the first to prepare this substance in the pure, crystalline condition, by salting out from its solutions.

In this form it contains 2 molecules of water, which, from its behaviour, appears to be present as water of constitution.

Since hydrosulphite is well adapted, not only for use in vat dyeing, but also as a discharge for many dyes which can only be discharged with difficulty, if at all, by other agents, many endeavours have been made to obtain it in a stable form. The preparation of the sparingly soluble zinc hydrosulphite, known in commerce as Hydrosulphite Z the French "Redo" is a zinc-sodium hydrosulphite only solved the problem in an imperfect manner. Later, however, the chemists of the Badische Anilin & Sodafabrik found that the stability of sodium hydrosulphite was greatly increased by merely expelling the water from the solid salt which is effected by heating it along with alcohol. A preparation of this kind, in admixture with caustic soda and glycerine, is sold as Rongalite B (Eradite B), and is a more efficient discharge than the ordinary salt. Sodium hydrosulphite can also be salted out, with caustic soda, in a very stable form.

The most important discovery, however, was that made by the chemists (Ch. Schwarz, L. Baumann, Sunder and Thesmar) of the Zündel calico-printing works, namely, that when combined with formaldehyde, sodium hydrosulphite is both more stable and a better discharge, since owing to its greater stability it does not exert its reducing action until it vaporises. This compound is sold as Hydrosulphite NF (Farbwerke Hoechst) and Hydraldite (Cassella).

Closer investigation of this substance revealed an unsuspected fact, namely, that it consists of two compounds formaldehyde bisulphite and the formaldehyde compound of a hitherto unknown form of sulphurous acid, the so-called sodium sulphoxylate, $NaHSO_2 . CH_2O + 2H_2O$, which is the most powerful reducing agent known. This is put on the market as Rongalite C (B.A.S.F.); Hydrosulphite C extra (M.L.Br.), and Hydraldite C extra (C.).

These preparations quickly attained considerable importance in discharge printing, especially after the discovery that their action can be greatly increased by small additions of a variety of substances. First of all, it was found by Baumann and Thesmar that even the highly resistant naphthylamine bordeaux can be discharged to a pure white by adding an alkaline solution of iron to the hydrosulphite discharge. Then it was discovered by P. Wilhelm, that the same result can be obtained in a more efficient manner by the addition of certain dye-stuffs, such as nitroalizarine, indigocarmine, etc. The best results are given by Setopalin, Patent Blue V and induline scarlet, added to the hydrosulphite; and mixtures of this kind are met with under the names Hydrosulphite NF conc special (M.L.Br.), Hydraldite special (C.), and Rongalite special (B.A.S.F.)

It has also been found that a large number of highly divergent substances, such as aromatic amines, ammonium bases, anthraquinone, 2·7 naphthol sulphonic acid (contained in naphthol R), solidogen,[1] are capable of augmenting the reducing power of hydrosulphite. Most of these substances probably have a catalytic action. In the case of anthraquinone, N. Planovsky has shown that it is transformed by hydrosulphite into a reduction product (probably oxanthranol), which is a more energetic reducer than hydrosulphite itself.

Finally, it may be mentioned that compounds of hydrosulphite or sulphoxylate with acetone have been prepared (M.L.Br.), which, in many instances, form better discharges than the corresponding formaldehyde compounds.

Kallab proposed to employ hydrosulphite as a bleaching agent in the narrower sense of the term, but this has not been adopted in practice. It can be used in just the same way as bisulphite, except that the bath is soured with acetic acid instead of sulphuric acid. In this case also, bleaching can be combined with blueing, the material being entered first into a suspension of indigo, and then into the bleaching bath. After remaining several hours in the latter it is exposed to the air for a short time and washed with a weak solution and finally with water.

Hydrosulphite is very suitable for stripping dyeings.

Tin salt, which also belongs to the discharges, will be dealt with along with the mordants.

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[1] A solidogen, the oxalate of anhydroform anilide, is sold as rodogen (M.L.Br.).

Cotton-Bleaching.

In the bleaching of cotton goods, the first question arising is the class of impurities present, and to what extent these are to be eradicated. In addition to the natural impurities, those artificially introduced in the dressing process, for example—have also to be considered. A piece of cotton fabric coming direct from the loom will always be cleaner and differently bleached than one that has been used as a backing in calico-printing, and therefore contains mordants, dye-stuffs, etc., besides the natural impurities of the fibre. Again, goods that are to be dyed in dark shades will require different treatment to those intended for pink, light blue, or white.

Finally, there arises the question whether the bleached material shall merely *appear* to be clean and white, or shall really be so. In the former event, the actual bleaching process may be dispensed with, the suitably prepared goods being blued, to mask the yellow colour of the raw cotton and turn the same into a fine, slightly bluish white. On the other hand, cottons to be afterwards printed must be bleached and cleaned in the most thorough manner possible, any residual impurities preventing the production of a first-class printed article.

Another point that must be borne in mind in carrying out the various manipulations the goods have to undergo is the nature of the fabrics themselves. For example, curtains, lace goods, and similar light fabrics must not be subjected to any tension or rigid pressure in the machines, and for this reason they must be handled tenderly, boiled as little as possible, washed loose, drained by squeezing between rubber rollers in the wringer, and so on. This also applies to raised goods, in which materials the lay of the nap has likewise to be considered, *i.e.* the goods must always pass through the machines in one direction, that of the pile, and never the other way about. In bleaching these goods, the operation of liming may be omitted, the lime having a hardening effect on the fibre, and impeding the subsequent operation of raising.

Formerly the bleaching of cotton was performed in such a manner that the goods, after a treatment with potash lye (from wood ashes) were decolourised by the action of atmospheric oxygen ("grass bleaching"), these two operations being several times repeated, and supplemented by a process of souring by immersion in sour milk. The bleaching process under these conditions lasted one and a half to three months in the case of cotton, and twice as long for linen goods.

This primitive method contained the germ of the modern processes of bleaching, all of which, however highly developed, comprise the three main operations of treatment with alkaline reagents (the so-called "bowking"), the actual bleach, and the employment of acids.

The substances to be removed from the fibre by bleaching are the natural and the adventitious impurities, the former comprising incrustating substances, fat, wax, yellow pigment, etc.; whilst the others include the dressing materials applied to impart greater stiffness to the fibre, and so facilitate the operations of spinning and weaving these are mostly mineral substances and also mordants, dye-stuffs, etc., in the case of piece goods that have been used as backing in calico printing.

It was quickly recognised that the first-named substances could be got rid of by boiling with alkaline reagents, and that the pigmentary matter of the raw cotton could be destroyed by means of bleaching powder, provided the greater portion of the mineral impurities had been previously removed. Consequently dressed cottons are either first steeped for some time in water, or, preferably, freed from the dressing by treatment with acids.

By boiling with lime the organic impurities can be converted into compounds that can then be readily dissolved and removed by boiling with soda and resin soap, the action of lime therefore being merely preparatory, and not actually one of cleansing; as a matter of fact, the goods are far darker in colour after liming than they were at first. The chemistry of this operation is still involved in some obscurity, probably the lime decomposes the pre-existing fats to form a lime soap, and converts the other organic matters into saccharine compounds or aldehydes, this view being countenanced by the discovery of Thies, who found that cotton treated with alkaline earth acquired strongly reducing properties. The acidulating ("souring") process after liming certainly decomposes the organic lime compounds, and enables the liberated fatty acids and other organic bodies to be brought into solution by the subsequent boiling with soda and resin lyes. At this stage the goods are already almost perfectly clean, and their faint yellow colour can now be destroyed by treatment with bleaching powder, the latter being then eliminated by the aid of an acid bath, followed by washing with water.

The foregoing is a brief sketch of the modern bleaching process, which therefore consists of the following operations: (1) boiling with lime; (2) souring; (3) boiling with soda and resin soap; (4) bleaching with chloride of lime; (5) souring.

That each of the operations is succeeded by a rinsing in water goes without saying.

Latterly, it has been found that the operations of boiling with lime and soda-resin soap can be advantageously replaced by boiling with soda lye. Many difficulties were, however encountered in introducing this alteration. In the first place, the lye must be weak, because strong lye mercerises and also weakens the fibre. Koechlin proposed to aid the action of weak alkali by steaming the steeped goods, but this method damaged the fibre, and the proposal was therefore devoid of practical value.

Nevertheless, it is possible to cleanse cotton in an excellent manner, without the slightest injury, by the use of strong soda lye. The credit of uniting the various factors here concerned into a technically practicable method belongs to H. Thies and E. Herbig, who found that impregnation with alkaline earths protected the cotton from mercerisation during subsequent boiling with strong soda lye, provided the treatment were performed in the absence of air, both in the kier and in the material.

The cleansing action of strong lye is so complete that the Thies-Herbig process must be characterised as the most important improvement made in the bleaching of cottons. Its value is further increased by the fact that it is also applicable to other kinds of vegetable fibres.

In connection with modifications of the bowking process, it may be mentioned that in France, for instance turkey-red oil, or a sulphide, is frequently added.

The proposal to add benzine and other detergent substances to the bowking liquor has not yet been adopted in practice.

The actual operation of bleaching has not suffered any important alterations, notwithstanding the numerous proposals made from time to time; and, for the most part, bleaching powder continues to be used, the method of application being that already described. It is, however, in many cases replaced with advantage by a purer form of sodium hypochlorite.

To turn now to the details of the bleaching process, it may be premised that cotton is bleached, almost exclusively, in the condition of yarn or cloth, the only exceptions being the bleaching of loose cotton for surgical wadding and jewellers' wadding the last named being usually dyed some delicate shade. The boilings necessary in bleaching would result in the entanglement and balling of the fibres if applied to the loose material, and the operation is therefore performed in the following manner: The material is first cleansed by a short boiling in a weak alkali, *e.g.* a 3 per cent solution of sodium silicate (water glass), and then bleached, if necessary, with hydrogen peroxide. When required for medicinal purposes, the cotton must be very slightly moistened with water, an object attained by very gradually drying the bleached material.

Bleaching Cotton Piece Goods.

The preparatory operations in this process consist of marking, sewing, gassing, and raising. Each piece is marked with a number, etc., so that it can be recognised after bleaching, the marking colour generally coal-tar being of a kind capable of resisting the bleaching agents used Then the pieces are sewn together, end to end, so as to make the entire batch of goods into one long piece or band. Next follows gassing, the object of which is to singe off the nap fibres standing up above the surface, since these would otherwise give the bleached material a woolly appearance, and also cause inconvenience in printing. The pieces may be gassed one or more times, and on either or both sides, by passing them rapidly over red-hot plates or cylinders, or over a row of non-illuminating gas flames.

In the case of plates, there is a difficulty in keeping them at uniform temperature throughout, owing to the cooling action of the cloth. This inconvenience can be counteracted by passing the goods through the machine again in reverse order. The plate system has the advantage of imparting a certain gloss to smooth fabrics; but it is unsuitable for patterned fabrics. The cylinder machine gives more uniform results; but the naked flame method is the best, especially for light goods.

Occasionally, as in the case of flannels, mollinos, etc., the goods are raised before bleaching; this is generally confined to the underside of the fabric though sometimes both sides are raised.

Goods intended for imitation of woollen mousselines are crabbed before bleaching.

It is a frequent practice, nowadays, to mercerise piece goods at this stage.

In the following bleaching operations the pieces are twisted in the form of a rope a method which possesses certain advantages though attended with various drawbacks.

Full Bleach with Lime and Resin Soap for Piece Goods.

(100 Pieces of 65 yards.)

1. **Steeping.** The goods are steeped in water for twelve hours, or even longer; this softens the dressing and other impurities present, and facilitates their solution afterwards. This preliminary steeping is, however, frequently omitted, especially when the goods are fairly clean already. On the other hand, if the pieces contain much dressing, or have been used in calico-printing in which event they will generally be strongly contaminated with alumina they will need steeping for some time in a weak solution of hydrochloric acid or sulphuric acid.

2. **Lime Boiling.** A milk of lime is prepared by mixing about ½ cwt. of quicklime[1] with 100 gallons of water, and passing the mixture through a sieve. Through this mixture the

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[1] About 1 lb. of lime per 100 yards of fabric.

goods are passed, and are then transferred to the bowking kier (Fig. 15), an iron vessel fitted with a wooden grating as false bottom, which is covered with a layer of sacking and then with the band of goods, the latter being packed together as closely as possible, in order to prevent them from being displaced in the course of boiling, and also to guard against the formation of cavities or hollow spaces between the layers, since otherwise the goods are liable to local overheating or scorching. The whole is next covered with wrappering, tamped down with rods,

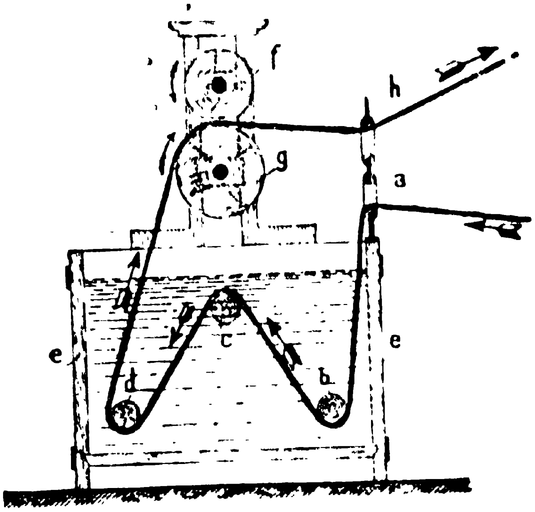

FIG. 15.

and covered with water, which is then raised to boiling-heat, and maintained at that temperature for six to fifteen hours, the kier being closed, and the pressure kept up to three or four atmospheres. The duration of this lime boiling varies according to the class of goods and the pressure employed, light pieces being finished sooner than heavy ones, and high-pressure accelerating the operation.

Apart from the various forms given to bowking kiers, they all contain, as a matter of principle, some arrangement for ensuring a continuous circulation of the bowking liquor (see Fig. 16).

When the operation is finished, the lime liquor is run off, the pieces being then swilled with water and transferred to a washing machine (Fig. 17). The lime must not be allowed to dry on the goods, or it will become very difficult to remove, nor should the limed goods be left exposed to the air, or the lime will absorb CO_2 and the expansion of the calcium carbonate so formed, will disrupt the fibres.

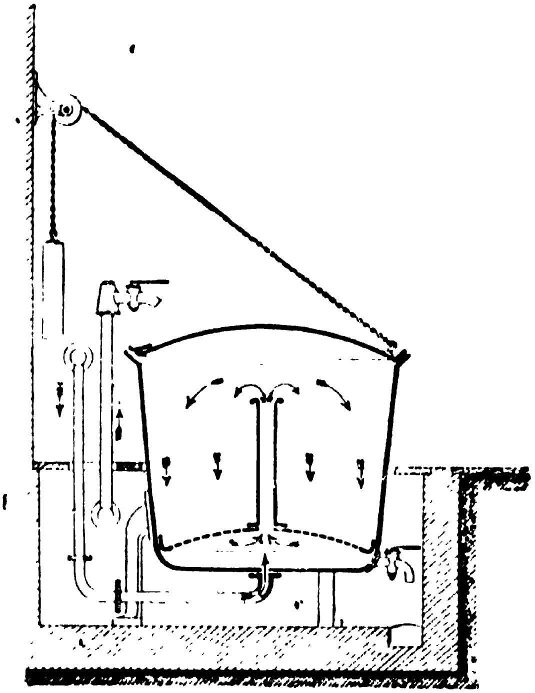

FIG. 16.

The washing machine used consists mainly of two wringer rollers, *c*, *d*, mounted on a strong frame, *a*, and driven by the pulleys, *b*, *e*; also of the roller *h*, which revolves in the water, the grating, *l* (separating the hanks in the case of yarn), and the two porcelain orifices, *i*, *k*, for the ingress and egress of the goods.

3. **Souring.**—The goods are passed through a vat contain-

ing 2 B. hydrochloric acid (sulphuric acid, though occasionally used, is less suitable, the insoluble calcium sulphate then formed being more difficult to eliminate than the soluble chloride) and is then left, covered up so as to exclude the light, in a wooden vat for about half an hour; or else the pieces are steeped for four to five hours in very weak (about ½ B.) acid. After this they are washed.

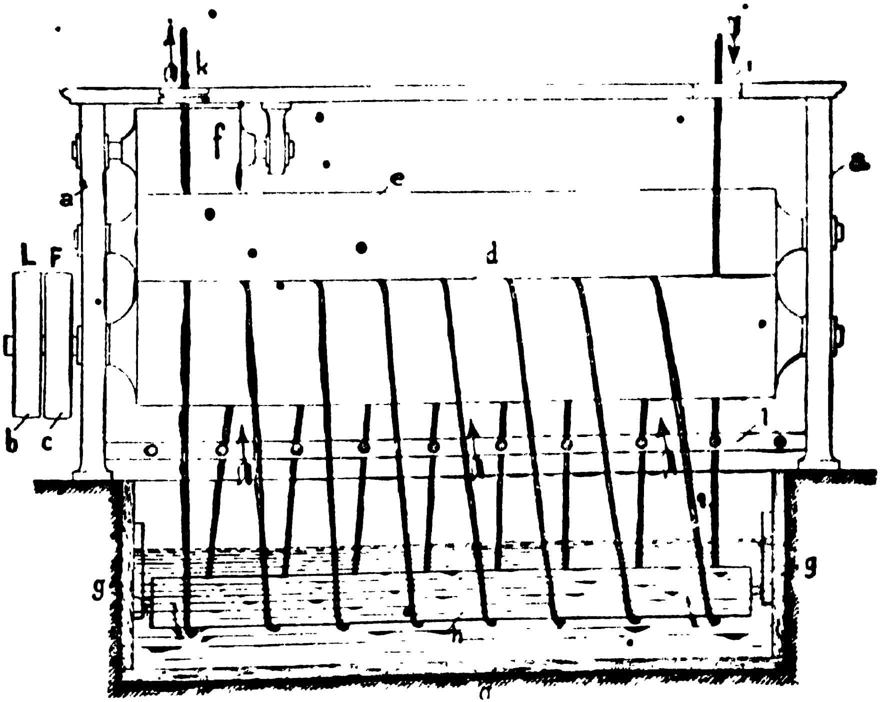

FIG. 17.

4. **Boiling with Resin Lye.** This operation is performed in the same manner as in lime boiling, and in similar kiers. The liquor is prepared by boiling 10 lb. of pale resin with 30 to 40 lb. of soda and 20 gallons of water for about six hours. This preparation is then diluted with about eight times its own volume of water, and the goods are boiled therein for about twelve hours, under a pressure of three atmospheres. After

running off the liquor, the goods are boiled with water, to remove the resin, and are finally well washed in the machine. If the goods were to be treated with cold water immediately after the resin boiling, the residual resin would adhere to the material and be difficult to remove.

5. **Bleaching (Chemicking).** The goods are impregnated with a clear, freshly made ¼° B. solution of bleaching powder, and then left alone in a dark place for half an hour or an hour; or they are steeped for six hours in a 0·3° B. solution of the same reagent. In either case the treatment is followed by a good washing.

6. **Souring.** To eliminate the rest of the bleaching powder, which would render the goods friable in time they are next passed through dilute (1° B.) hydrochloric acid, and left exposed to the air for half an hour; or they are steeped for several hours in a more dilute acid, the addition of bisulphite, as "antichlor," being advisable. Finally the goods are washed until they no longer give an acid reaction with litmus.

Full Bleach for Piece Goods in Soda Lye.

1. The goods are steeped in water for at least twelve hours.

2. They are next boiled for fourteen hours in 2 to 2½° B. soda lye, without pressure, to prevent the impurities being fixed in the material. Washing follows.

3. Souring, by immersion for four or five hours in ½° B. hydrochloric acid, succeeded by washing.

4. Second lye boiling, with lye of the same strength as before, for sixteen hours, but under pressure: washing.

5. Souring as before; washing.

6. Chemicking. The goods are steeped for six hours in clear, freshly prepared 0·3° B. bleach liquor, and afterwards washed.

7. Souring as before, followed by washing.

If the goods are to be dyed with alizarine rose-red, they must be bowked with lime previous to the first lye boiling.

The Thies and Herzig Full Bleach for Piece Goods.

(30 cwt. of Cotton.)

1. Souring, partly for removing the mineral impurities, partly for separating them from their organic combinations. A modi-

fication of the souring process, recommended by Thies and Herzig, *viz.* adding a little hydrofluoric acid to the bath and then steaming the goods, has not been found suitable in practice. When the goods are clean this preliminary treatment may be omitted.

2. The goods are steeped all night in a ½ per cent. soda lye at 50° C., to remove adherent matter, dried sap, etc. If the stuff is very unclean this operation is repeated.

3. The next process is washing in water containing an alkaline earth salt, which facilitates the removal of the alkali and deposits insoluble alkaline earth in and upon the fibres. Fifty grms. of 25 per cent. magnesium chloride are taken per 1000 litres of water—*i.e.* 0·0005 per cent.—or correspondingly less in the case of hard water. The pieces are then put through a wringer, so as to leave in the material only about its own weight of water.

4. Bowking in the kier by steam heat, at a temperature of over 100° C. This takes up to two and half hours, according to the size of the kier, and is performed as a preparation for the following boiling in strong soda lye. The latter being introduced in a hot state, the mercerisation of the goods is prevented, and the steam expels the air which would otherwise enable the strong alkali to corrode the fibre.

Moreover, the conjoint action of the alkaline earth and heat on the impurities in the cotton results in the formation of reducing bodies, which are easily removed in the subsequent lye boiling, and besides counteract the oxidising action of the latter.

5. The goods are suffused with hot lye, at a temperature exceeding 100° C. This solution is prepared from 1 cwt. of 98 to 99 per cent. soda, causticised with lime and diluted to 110 to 120 gals., 20 lb. of resin being then boiled therein. This gives a lye of about 5 to 7 per cent. strength. The specified weight of cotton occupying a space of about 140 cub. ft., this quantity of lye will only be just sufficient to thoroughly impregnate the material. In the older methods the use of strong lyes was prohibited for economical reasons, since to cover the goods requires about 2 to 3 times their own weight of lye.

The circulation of the lye and steam is maintained by the pump, *d* (Fig. 18), which draws and delivers them into the vessel, *c*, thence into the heated vessel, *b*, from which they return to the kier, *a*, where the goods are situated. The vessel, *c*, contains a perforated pipe, *e*, through which a part of the steam escapes into the open air at *f*, thus compensating for the dilution produced by the saponification process within the vessel, and maintaining the uniform strength of the lye.

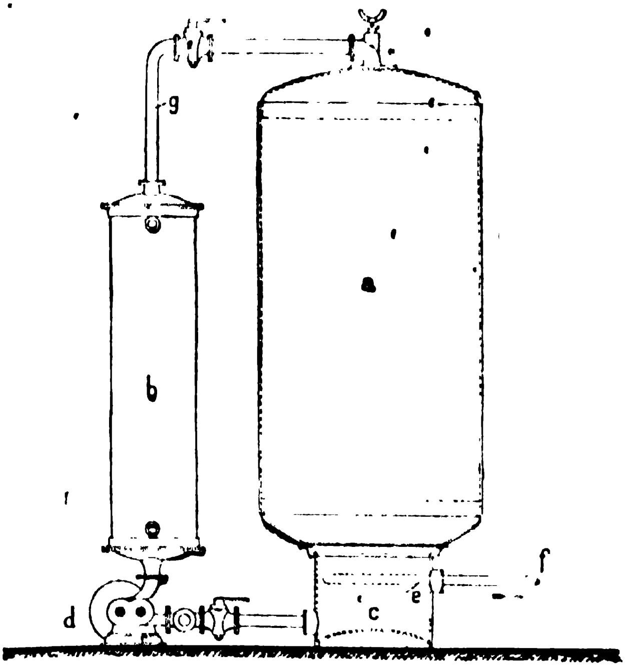

FIG. 18.

At the end of about three hours the goods are washed with boiling water in the kier.

6. **Chemicking.** This operation is performed with bleaching powder as usual, or with pure sodium hypochlorite, the only difference being that the liquors are merely one-third the ordinary strength.

7. Souring, as in the first operation.

The principal advantages of the Thies-Herzig process consist in a saving of about 40 per cent., as compared with the ordinary method (lime and resin soap), more rapid performance, absolute purification and unimpaired strength of the bleached goods. Indigo blue can be more readily discharged than usual when the goods have been bleached by this method.

Whichever method of bleaching has been employed the goods are afterwards loosened in a machine, then spread out and hot-calendered, or tentered, if necessary, after which they are sorted and shorn. The latter operation is performed in order to remove the nap from the surface of the cloth, the short hairs composing same being first raised by brushing and then cut off by revolving cutters. A final brushing completes the process. Of course this operation is omitted in the case of goods in which the pile constitutes an essential feature of the weave.

Bleaching causes the goods to loose 8 to 11 per cent. in weight, and even a loss of 20 per cent. is not extraordinary.

In order to obtain perfect results, every stage of the bleaching process must be supervised with extreme care, the more so because a batch represents a considerable sum of money. The progress of the operations is checked by taking samples at intervals and dyeing them with alizarine, this test revealing any spotting produced by lime, resin, or bleach. Stains due to the formation of oxycellulose, have a rusty-brown appearance, but can mostly be got rid of by treatment with ammonia or soda.

The bleached goods are washed out in separate machines and stored away from possibility of contact with chemicked or soured pieces. Great care must be taken to avoid rust stains, these forming the most unwelcome of all the bleacher has to fear. With this object the kiers must be kept perfectly clean; no accumulations of liquids must be allowed to collect in the steam and water-pipes, etc. Should they occur, these stains may be taken out with oxalic acid. Chemicked goods must not be allowed to touch iron, or a local catalytic action will be set up which decomposes the bleaching agent and oxidises the cellulose. Dye-stains, such as the alizarine red on backing pieces from the calico-printers, can be discharged by bleaching with potassium permanganate.

Bleaching Cotton Piece Goods Wide Open.

The drawback in bleaching cotton goods twisted in the form of a rope is that the delicate surface of many fabrics, such as twill, damask, moleskin, etc., is liable to suffer from the formation of creases, which are afterwards difficult to obliterate. On this account, many attempts have been made, of late years, to devise means of putting the goods through the various operations of the bleaching process, without the necessity for twisting and untwisting again.

Without going into particulars of all the various methods proposed, it may be mentioned that many of them are based on the principle of soaking the fabric with lye, and passing it, in the wide open condition, through a closed chamber in which it is exposed to the action of steam under low pressure. For this purpose a number of machines have been put out on the market, such as those of Bentz, Edmeston & Grether, Endler & Welter, Gebauer, Tagliani, Rigamonti, and others. The Endler & Welter machine consists chiefly of a quadrangular wooden casing, which is open underneath and dips into a sealing trough containing lye and a little bisulphite and arranged in such a way that the goods are passed through the lye on their way into and out of the chamber formed by the casing. While passing through this latter, under the slight pressure due to the sealing liquid, they are exposed to the action of steam, being suspended to hang in folds and carried along by a special conveyor device, to be discharged, completely bowked, at the further side of the machine. Condensation of the steam in the chamber is prevented by using radiators. The whole operation only lasts about half an hour, but of course the use of the method is confined to certain goods, being unsuitable for others.

In other methods of the same type the bowking appliances are provided with devices which hold up the goods at intervals so as to expose them longer to the action of steam. This very useful principle, which was first advanced by Weiss-Friess, is embodied in the Tagliani apparatus.

Another principle of wide-open bleaching is that, in the bowking stage, the lye is forced through the fabric spread full width on rollers, either by the action of a suction pump which draws the liquor through in an axial direction, or else by a force pump which drives the liquor through from the inside. In the Mather and Platt method, which is extensively used, the fabric, after traversing the bowking kier, is wound on a roller, at one end of which a perforated disc fits closely against the edge of the goods. On the whole being placed in the boiler and the perforated disc connected to a pump, lye is drawn through the fabric, axially, throughout the operation, whilst the roller can be kept revolving. Neutralising and chloring can be effected in a similar manner.

Thies and Gebauer insert laths between the layers of fabric in winding, because if too tightly wound, it is difficult to force the liquor through. According to the same inventors, the bleaching process can also be carried out by steaming the rolled up fabric that has previously been steeped with lye.

Full Lye Bleach for Yarns.

1. The goods are steeped in water for about ten hours, but if the yarn be fairly clean this may be omitted.

2. They are next boiled for fourteen to sixteen hours in lye of 2 to 2½ B. strength, followed by washing.

3. The next stage is souring, by several hours' immersion in ½ B. hydrochloric acid, succeeded by washing.

4. Chemicking. The goods are steeped for about five hours in a 0·15 to 0·2 B. solution of bleaching powder, and then washed.

5. Second chemicking in the same way.

6. Second souring, as before.

7. The yarn is softened by steeping for some time in a hot solution of soap, and is then washed once more.

This method is very similar to that employed for piece goods. Modifications of the process are practised in some places, and occasionally the other methods described are applied to yarns.

Partial Bleaching.

As already stated, it is not always necessary to bleach cottons fully, this being done only when the goods are to be dyed in light shades or printed, whereas for dark shades of dyed goods bleaching would in many instances be a superfluous operation, and one likely to injure the colour in the case of turkey-red dyeing.

Cottons for half bleaching are bowked with lime or soda, soured, and washed. Yarns are boiled, without pressure, in a very weak soda lye, and then boiled off and rinsed; occasionally a simple boiling in water is sufficient. In many cases, soaping (see turkey-red oil) is a sufficient preparation for dyeing, especially with basic dye-stuffs, in which case the soaping can be combined with the tannin treatment. Goods to be dyed with aniline black do not require any cleansing at all.

White goods are first boiled with alkali, then chemicked, and blued with ultramarine. In the case of piece goods this is done in the dressing process, but with yarns the ultramarine is applied in suspension in a warm soap bath. Latterly, however, owing to the ease with which irregularities occur in blueing with ultramarine, this pigment has frequently been replaced by methyl violet applied in an alum bath.

Finally, it may be mentioned that fabrics with dyed fancy threads (*e.g.* dyed turkey-red) require special care in bleaching. Boiling with soda lye must be avoided, and the best plan is to boil with soap (and perhaps a little carbonate of soda as well), under moderate pressure. In chemicking, the coloured portions should only be left in the bleach solution for a short time, and then taken out and washed.

Out of the many methods proposed for bleaching cottons, the following may be mentioned:—

G. Hertel's Bleaching Process (German patent, 75,435, 30/3/93). The material to be bleached is impregnated with a ½ to 10 per cent. solution of turkey-red oil (according to the desired effect), the excess being removed by wringing or draining in the hydro-extractor, and the goods boiled with 1½ to 2 per cent. of caustic soda for six hours under pressure, after which they are rinsed, slightly soured, washed, lightly soaped, rinsed, and dried.

This method is claimed to be specially suitable for yarns to be dyed rose-red by the Erban and Specht process, and also for

Mako cotton, which hitherto could not be bleached except by the aid of very strong chemicking baths. It is not new, because in France (Rouen, for example) it has long been the practice to cleanse cottons that are to be dyed in delicate shades, by boiling with lye and a sulpholeate. A product of this kind is sold under the name "Fankhausine". Sulpholeates (*e.g.* "monopol" soap) form very useful additions to bowking liquors, since they readily moisten and cleanse the cotton, so that the duration of boiling can be reduced, and the goods may be allowed to cool down during this treatment.

The Mather and Thompson Continuous Bleaching Process. The characteristic features of this process are that, after certain preparatory treatment, such as lye boiling, souring, etc., the goods are passed continuously over a series of rollers, and also through a chamber filled with gaseous carbon dioxide for the purpose of liberating hypochlorous acid and thereby increasing the activity of the bleaching powder. The goods are passed in succession through warm water, bleaching powder solution, the carbon dioxide chamber, cold water, warm soda solution, water, a second chemicking bath carbon dioxide gas, water, dilute hydrochloric acid, and, finally, water.

Electrolytic Bleaching Process. The method is usually associated with the name of Hermite, who was the first to propose the preparation of a bleaching liquor by the electrolytic decomposition of magnesium chloride. The most important features of the process have already been described in dealing with sodium hypochlorite.

Linen-Bleaching.

The bleaching of linens is conducted on the same principles as in the case of cottons, the impurities being removed by boiling with lime or soda, and the colouring matter by the aid of bleaching powder.

The fibres are, however, more difficult to decolorise than those of cotton, owing to the larger quantities of impurities present, the amount and quality of which depend on the method of retting pursued. Consequently, this last-named process should be performed with special care.

Moreover, flax fibre is more susceptible than cotton, and on this account the various reagents must be used in a weaker condition and applied over and over again. The chief cause of the difficulty in bleaching flax resides in the brown substances, known as pectin bodies, contained in the fibre, since they cannot be destroyed by the unaided action of bleaching powder but require the assistance of the grass bleaching process. Apparently these bodies are not destroyed by the bleaching agent, but are merely converted into a form more soluble in alkalis.[1] A single vigorous treatment with bleaching powder does not suffice to remove the pectin bodies; neither is this treatment advisable, as it would certainly attenuate the fibre. The conversion of the pectin bodies into a soluble form is therefore a matter of repeated attacks with bleach, assisted by interposed treatments with alkaline baths, and supplemented by grassing.

Apart from the repetition of the various operations and the recourse to grassing, the process of linen-bleaching differs from that for cotton in that the goods are kept in motion during the treatment in the chemicking bath (though this is also done with cotton goods in some works), and are subjected to friction between two fluted boards in order to get rid of the particles of adherent brown matter.

Flax is bleached either as yarn, twist, or in the piece, and the process is divided into four classes—quarter, half, three-quarters, and full bleach, according to the degree of purification produced. The loss in weight ranges up to as much as 18 per cent, or occasionally as high as 25 per cent., and ends at the half-bleach stage. The entire operation takes about three to six weeks.

The boiling is effected in open and in low-pressure keirs; the chemicking and souring are performed in a special manner, *viz.* in a series of (usually) three stone or wooden tanks containing respectively dissolved bleaching powder, water, and dilute hydrochloric acid. The yarn is suspended on pegs, which are mounted on a frame running on rails over the top of the tanks. Sometimes the pegs supporting the yarn are fitted with cogwheels which engage in one another and cause the yarn to turn round and round in the bath liquor.

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[1] The Muller process (already described) for obtaining pure cellulose from crude vegetable fibres, is based on this reaction.

After a short time the entire frame is lifted out of the bath and transferred to the next tank, where the yarns are washed. In the same manner they are conveyed to the third tank, where they are soured, and are finally washed in a fourth vessel, or returned to the second tank for that purpose.

Piece goods are first moved about in the chemicking liquor for some time, and then left to steep therein, though more usually the movement is continued and extended over a longer time.

For grassing the yarns and piece goods are spread on the grass in summer, and turned at intervals; in winter they are hung on sticks or frames. Naturally, the bleaching action is stronger in the summer, and becomes apparent after the lapse of only a few hours. Eggemann proposed to expedite grass bleaching by first slightly blueing the goods with indigo, in order to ensure the absorption of the more active blue light rays as well as the yellow ones.

Well-bleached linens should be white all through, and should not stain when treated with an alkali, such discoloration indicating imperfect removal of the pectin bodies.

The details of linen-bleaching naturally vary in different localities. The following description applies to the method as pursued in Silesia :—

Full Bleach.—

1. Boil for nine to ten hours, or longer, according to quality, with 10 per cent. of soda, under gentle pressure.

2. Chemick with a bleaching powder solution, containing 1 per cent. of active chlorine ; wash and sour.

3. Treat in hot (50° C.) soda solution in an open keir ; wash.

4. Grass for two to three days (in summer), turning once.

5. Chemick for several hours in a weak solution of bleaching powder, evolving only an almost imperceptible odour of chlorine.

6, 7, 8. Repetition of 3, 4, and 5.

9. Weak soaping in circular vat, the soap solution being admitted automatically, flowing through the yarn, collecting underneath, and returning to the goods after passing through an upcast pipe.

Piece goods are treated in the same manner, except that the operation commences with a lime bowking.

It should, however, be borne in mind that working on any invariable lines is an impossible matter in linen-bleaching, the method of treatment being wholly dependent on the quality of the goods and on the effect to be obtained.

Jute-Bleaching.

Almost every known bleaching agent has been tried on jute, from which circumstance it will be evident that a perfectly satisfactory method of bleaching this fibre has still to be discovered.

As a rule the work is confined to a bleaching in the restricted sense of the term, sodium hypochlorite being chiefly used. Under these conditions a supplementary treatment with dilute bisulphite will prove beneficial.

The method of bleaching jute by alternate treatment with potassium permanganate and bisulphite, though rather expensive, furnishes good results, and the loss in weight is small. In some cases the two methods are combined, the jute being treated with bleaching powder first, and then with permanganate and bisulphite.

Jute, being very susceptible to the action of alkalis, should only be treated with such as are of a very mild character, like sodium silicate, borax, etc.

However, this fibre is generally used in an unbleached condition, either in its natural colour, printed, or dyed (or both).

Hemp-Bleaching.

Great difficulty is experienced in bleaching hemp in a thorough manner, and the fibre is generally used in the unbleached state; in fact, only the yarns intended for making up into string are bleached, the operation being effected by the aid of bleaching powder after a preliminary cleaning with sodium silicate.

Ramie-Bleaching.

As already mentioned, the process used in Europe for bleaching ramie is almost identical with that employed for cotton;

only, in the chemicking especially, greater care is necessary to ensure the protection of the fibre.

Scouring and Bleaching Silk.

The purification of silk consists in removing the gum and colouring matter present in the raw material. As, however, these mainly reside in the bast layer, all that is necessary in most cases is to get rid of this latter by the operation known as scouring, or decorticating.

The bast layer gives the silk a hard, rough character, which prohibits its use in a raw state, except in very few instances. As a rule, silk is desired to exhibit all its valued properties, such as softness, lustre, etc., and on this account must be freed from the bast, the more so because raw silk cannot be dyed so permanently as when scoured, the reason for this being that the dyes are then absorbed by the bast, which afterwards yields them up more readily when washed.

Removing the bast entails considerable loss in weight, amounting to 18 to 22 per cent. in the case of Chinese and Japanese silks, and 25 to 30 per cent. in European silks. On this account it is often customary to scour the silk only to such an extent that the loss amounts to about 6 to 8 per cent., the endeavour being at the same time to impart to the product a portion at least of the valuable properties of scoured silk. The resulting product is known as "souple" silk, and is used as a weft. In treating this article, the fact that it will not stand warm soap or alkaline baths must be borne in mind; in fact, if only left to lie in a moist condition, it sheds part of its bast layer spontaneously, this effect being recognised by the formation of lustrous spots. It must therefore be either dried at once, or else dyed and dried; should immediate dyeing be impracticable, the silk must be left in water.

The silk is scoured in hank form, as grège silk, or also after weaving, the operation being performed by the aid of soap and soda. True, soap alone is best, and that too of good quality, devoid of free alkali or smell, and being readily soluble so that it can be afterwards easily washed out of the silk. Potash soap is better than soda soap for this purpose, and, in fact, soda does not form a good addition to the scouring bath, owing to its tendency to make the silk harsh. However, for the sake of cheapness, a mixture of soap and soda is frequently used, and the cheaper souple silks are even scoured with soda alone.

For better qualities it is essential to employ nothing but soap, an addition of soda being inadmissible, except for the purpose of softening the bath water, since the lime soap, otherwise formed, would be deposited on the fibre and dirty it, or at least spoil its sheen. It is therefore necessary, in scouring silk, to entirely prevent any deposition of lime or magnesia soap on the fibre. Should the raw silk not be entirely free from mineral matters (*e.g.* dust) it is advisable to wash it, first in slightly acid water and then in pure water, before scouring. The same consideration must also be borne in mind in washing the silk after scouring.

Two scouring baths are generally required: the one containing 25 to 30 per cent. of soap, the second 20 per cent., calculated on the weight of raw silk treated.[1] The grège is treated in the first bath for about ten minutes or longer, according to the quality, at a temperature rather below 100° C. The bast swells up, making the silk sticky, and then dissolves, leaving the lustrous internal thread of the silk exposed. A sojourn in the second soap bath then completes the removal of the bast. Silk that is to be dyed in delicate shades is passed through a third soap bath, and finally rinsed with fresh water.

The first bath can be used seven times over, but will then be so full of sericin as no longer to be applicable for this purpose, though suitable for use as "bast soap" in silk dyeing. The second bath, which contains a smaller proportion of sericin, is advanced to the dignity of first bath, a fresh solution being prepared in its place.

Of course, it is not feasible to treat all kinds of silk in exactly the same way, some being more easily freed from bast than others; and in point of their ability to stand the action of the scouring baths considerable differences exist, Milanese trame silk being particularly ticklish to handle. In fact, this silk must not be left in the bath more than ten minutes, and should the bath liquor contain any pre-existing sericin, the silk will be rendered "lousy". Such silk exhibits, when dyed, numerous light patches, due to the disintegration of the silk thread; the appearance may, however, be improved by treatment, first with soap and afterwards with weak hydrochloric acid.

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[1] The following recipe from a practical source may be cited as an example of other methods of scouring silk. The silk is treated for three to four hours at 70° to 80° C. in a bath containing 6 parts, by weight, of Marseilles soap and 1 part of soda per 1000 parts of water—the latter previously softened—after which the material is washed, soured with weak hydrochloric acid, and rinsed.

In the case of *loaded* silk, the removal of the bast is almost impossible to effect in a satisfactory manner, owing to the inevitable formation of metallic soaps. Before proceeding to the scouring process the loading materials must therefore be eliminated by treatment with a cold 1 per cent. solution of hydrofluoric acid or a cold-saturated solution of oxalic acid.

After the silk has been scoured it is stretched, chevilled (smoothed), lustred, bleached, loaded, and dyed. The first three operations are performed with the object of rendering the silk as soft and lustrous as possible. Stretching consists in repeatedly pulling back the silk threads when stretched taut be-between two rods, and is effected either by hand or in a machine.

Smoothing is effected by winding the silk upon itself, by hand or in a machine, whereby the separate threads are smoothed by mutual friction. (Machines for this purpose are illustrated in Knecht, Rawson, and Loewenthal's *Handbook of Dyeing*.)

Lustring or glossing consists in imparting the maximum lustre to the silk by a combined process of stretching and steaming.

Bleaching is only practised when the silk is required to be white or to be dyed in very light shades. Sulphurous acid is the agent employed, and the method has been already described in dealing with that reagent.

Loading.—In the case of white or very light-coloured silks, a dressing of tin chloride (see Chap. III.) is applied before dyeing, but dark-coloured silks are loaded in the dyeing process, or afterwards, by the aid of tannic acid.

Scouring silk in the piece is a method increasing in favour on account of the advantages resulting from weaving the threads in an unscoured state. For example, raw silk is better able to stand friction, and is more elastic than when scoured, so that it is less liable to break in the loom; and again, the almost inevitable dirtying to which the threads are exposed in weaving is merely superficial in raw silk, and is readily removed in the subsequent scouring.

The operation is performed in a continuous manner by passing the pieces, wide open, over rollers and through vats containing hot solutions of soap and soda (*e.g.* 6 parts of soap and 1 part of soda per 1000 parts of water); they are heated first to 70° or 80° C., then to 100° C. The operation takes a half to three-quarters of an hour, or sometimes longer.

Half-silk (cotton and silk) goods are scoured in the piece exclusively, and must be gassed beforehand. Half-silks to be dyed dark shades contain raw (unbleached) cotton, and therefore, except when the proportion of this is very small, the goods must be put through a strong scouring bath (containing 3 to 5 per cent. of soda, calculated on the weight of the goods), the operation in this case lasting one and a half to two hours.

According to a process patented by the Badische Anilin & Sodafabrik, the fabric should be treated for about ten minutes in a cold and fairly strong lye, glucose being added to the liquor in order to prevent the silk being weakened, on the one hand, and the cotton from shrinking, on the other. This treatment scours the silk and at the same time cleans and mercerises the cotton.

Half-Scoured or Souple Silk.

To prepare half-scoured or souple silk, the silk is first cleansed by treatment in a weak, lukewarm soap bath, which at the same time softens the bast. After this it is immersed in a 10 per cent. bath of potassium nitrite, strongly acidified with sulphuric acid for an hour, or for about a quarter of an hour in warm dilute *aqua regia* (nitro-hydrochloric acid): in the first case the colour turns grey, in the second green. Then, after being treated in a bath of soap, plus a large proportion of soda, it is sulphured three times, six hours each time, in a damp state, the hanks being turned after each treatment. The next stage is rinsing in water acidified with sulphurous acid, followed by the actual process of softening, the hanks being steeped in a hot (90° to 100° C.) 5 per cent. solution of potassium bitartrate, and an aqueous solution of sulphurous acid (the condensed droppings from the sulphuring chamber) until the threads are exposed, though this is not perfectly visible until they have been drained. According to the quality of the silk, the treatment lasts an hour or more.

Some dyers use a bath of bitartrate and hydrochloric acid, or magnesium sulphate, in which latter event the loading of the silk is effected at the same time; the feel of the silk is, however, best when sulphurous acid has been used. When the silk is to be dyed in dark shades the softening process may be performed with tannic acid in the dye bath.

Bleaching and Scouring Tussah Silk. Attempts have been made to bleach Tussah silk by almost every known bleaching agent. The operation is a difficult one, and is therefore omitted except when the silk is to be dyed in light shades. For the most part it is woven in its natural colour.

The best bleaching agents for this fibre are the peroxides, the material being treated for an hour or so in a bath containing 50 to 100 per cent. of barium peroxide at about 90° C.; or else with hydrogen peroxide in conjunction with sodium silicate.

Scouring is also a more difficult process with Tussah than with true silk, and entails more time and the use of stronger soda baths.

Washing and Bleaching Wool.

Whereas the entire series of operations concerned in the purification of cotton are comprised in the term "bleaching," a distinction is made, in the case of wool, between the actual bleaching process and the preparatory cleansing operations, the latter being termed "washing".

As it comes from the sheep, wool is contaminated with so many impurities that washing is the first treatment necessary, it being impossible to spin unwashed wool, though raw cotton can be spun without question.

Woollen yarns and piece goods, though freed from the natural impurities of the fleece, nevertheless contain impurities, consisting of the fatty matters added to the wool to facilitate spinning and weaving, in addition to dirt acquired by contact with dirty machinery, dust, and the workman's hands. Consequently, the washing of these goods is performed in a different manner to that employed for the raw wool.

Bleaching, as applied to wool, is restricted to yarn and piece goods, and plays a far less important part than in the case of cotton, the great bulk of manufactured wool never being bleached at all.

Though in this country it is a common practice to wash the sheep before shearing, this is rarely done in the case of foreign wool, and when practised has always to be supplemented by the usual wool-washing process, except for low-grade wools such as Hallina. This supplementary washing should be performed as soon as possible after shearing, since delay only increases the difficulty as experience has shown in the case of fleece-washed foreign wools.

The washing to which the wool is subjected in wool-washing establishments is a far more important operation than fleece-washing, its object being to secure the removal of all the impurities comprised in the term "grease". For this purpose use is made of alkaline substances—soda, potash, soap, Quillaya bark (*Quillaya saponaria*), ammonium carbonate, and stale urine. Caustic alkalis, however, must be carefully avoided, owing to their known corrosive action on wool fibre.

The oldest known detergent for wool-washing is stale (putrescent) urine, which, when diluted with about five times its own bulk of water and used at medium temperatures, cleanses the wool very well. The real active ingredient is ammonium carbonate, liberated by the decomposition of the urea. Despite its unpleasant smell, this detergent is still used in many small works.

Ammonium carbonate itself is an excellent detergent for wool, but is still too dear for practical use, the field being left almost exclusively open to soap and soda (or potash). Usually a mixture of the two is employed, the proportions being regulated according to the quality of the wool and the hardness of the water. The coarser the wool the larger the proportion of soda, and it will be readily apparent that hard water requires more soda than soft water, it being necessary to throw down the lime and magnesia as carbonates, in order to prevent their deposition, in the form of fatty acid compounds (soaps), on the wool. The carbonates of these alkaline earths come down in the form of powder and can then be easily washed out of the wool, which is not the case with lime and magnesia soaps; moreover, the formation of the latter entails a certain waste of soap, and therefore hard water should first be softened.

Wool of low quality, such as is used for making coarse fabrics, rough blankets, etc., is washed with soda alone, for the sake of cheapness; but worsted wools are washed solely with soap. Wools for carding are washed with a variable mixture of soap and soda, averaging 4 to 5 parts of ammonia-soda and 1½ to 2 parts of soap per 1000 parts of water. Soda soon roughens wool, and the temperature should not be allowed to exceed about 50° C. when this alkali is used. Its employment is nevertheless essential for fine carding wools, since fine wools are more difficult to cleanse than the coarser kinds, and a larger proportion of soap would cause the fibre to shrink and thus unfavourably influence the wool for the purpose in view.

The exact proportions of soap and soda can only be determined by practical experience, since each kind of wool behaves differently in the washing. Hence care should be taken never to wash different sorts of wool together; and the sorting of wool previous to washing must be performed with great caution.

Other proposed adjuncts to the above-named detergents are common salt, sal ammoniac, olein (as an emulsifier), etc., but none of them have made any headway in practice. Patented detergents of undisclosed composition, sold under fancy names for wool-washing, should be avoided in any case, since they are either worthless, or could be prepared by the washer himself at a much lower cost. For the most part they consist of a larg proportion of soda and a very little soap, and are therefore generally recommended for washing with hard water.

The Washing Process.—The wool is first carefully sorted and freed from burrs, which latter would injure the fibre if not removed. It is then put in the washing machine, the so-called "leviathan," shown in Figs. 19 and 20, which consists of a series of tanks (generally four or five), the first of them containing the detergent solution, the others filled with warm clean water. The actual cleansing of the wool therefore takes place in the first tank, the temperature of which is kept at about 50° C., whilst the others serve for rinsing the purified charge. Each tank is fitted with cranked rakes, which move the wool onwards, and between each two adjoining tanks is mounted a pair of heavy ringer rollers, which take the wool from the elevator and, after expressing the superfluous liquor, deliver it to the next tank. The best type of leviathan washer is that of A. Déru, shown in Fig. 19, the chief advantage of this type residing in the excellent elevator and wringers, which latter work under a pressure of about eighteen tons. By this means the wool is squeezed in a very thorough manner and the transference of dirty scouring liquor into the rinsing tanks is reduced to a minimum.

Fig. 19, shows the elevator and the submerging roller of the second tank of the Déru machine, the former consisting of two toothed wheels *a*, rotating about a shaft *b*, mounted at *d*. Bearings *e* support the pins *f*, which carry the paddles *g*, and the attached zinc forks *h*. The movement of the forks which carry the wool is effected by the sliding of the rollers *i*, *k*, on the tracks *l*, *m*, and the wool is delivered between the rollers *o*, *p*, whence it passes at *q* into the wheel *r*.

Fig. 20 shows the manner in which the wool is worked in the Demeuse machine by the crank rakes *b*, *c*, to the elevator *d*, and from the latter to the wringer rollers *f*, and thence to the creeper *h*.

The scouring liquor in the first tank will, of course, remove the bulk of the impurities, and will have to be drawn off after a certain time. In order to utilise the liquors to the utmost, that from the second tank is then run into the first one, its

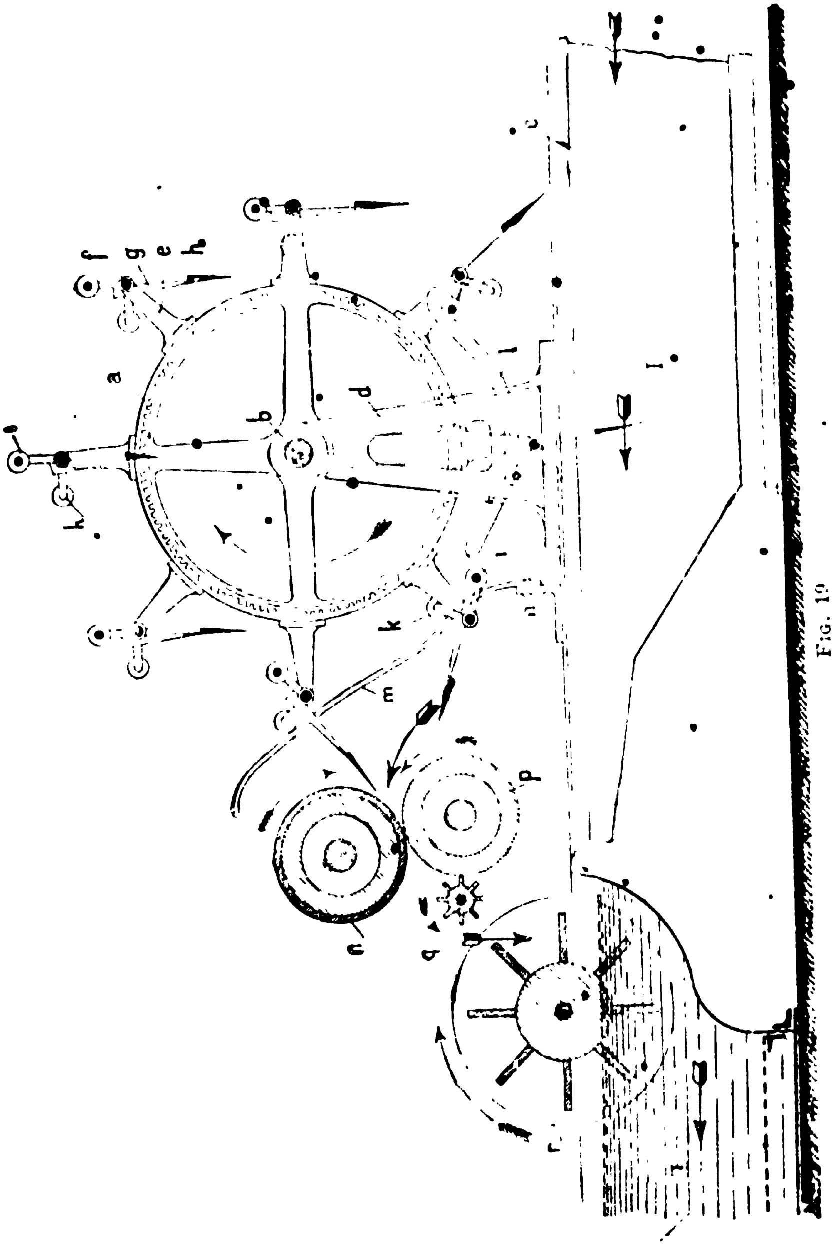

FIG. 19

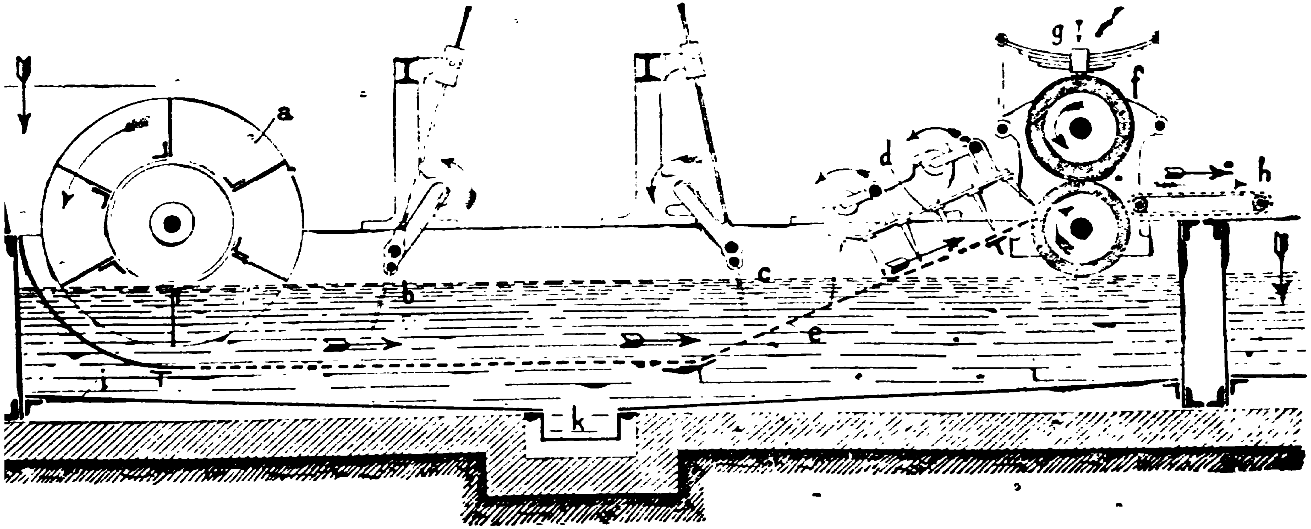

FIG. 20.

place being taken by that from the third tank. This transfer is effected by means of an injector.

When properly washed, wool still contains about 1 per cent. of fat. In some washing mills a larger proportion is designedly left in the wool, but this is not advantageous to the purchaser.

In washing worsted wool, it is sometimes the practice to incorporate combings, as a cheap and pure adjunct which unites well with the wool and cannot afterwards be detected therein.

The spent liquor from the washing machines is run into a collecting tank, through a vertical iron grating which keeps back any accompanying wool fibres. These latter, though very dirty, can be washed and sold as inferior wool. The liquors are then passed through a series of settling tanks, where the bulk of the suspended impurities is deposited, after which the liquid portion is either run off or treated with sulphuric acid or lime for the recovery of the contained fatty acids. When acid is used, the fatty acids are obtained in a free state, but when lime is employed they are in the condition of lime soaps, which must then be decomposed by an acid. The former method is most in use, and is best performed in the warm. The recovered fatty acids are purified by pressing, smelting, and bleaching.

This recovery of fatty acids pays only in the case of large establishments, and even in such works the acids are sold in their crude state to the soapmaker.

Latterly, the recovery of wool fat from the washing liquors is practised, the liquor being treated in a centrifugal extractor, which retains this fat. The latter is then purified by repeated meltings, boiled with water, and kneaded with water to form the commercial product lanolin, which is largely used as a salve, owing to its capacity for penetrating the skin. Liebreich was the first to recommend it for this purpose.

The soapy water left in the recovery of wool fat can be used over again as scouring liquor.

Finally, the potash in the yolk of the wool can be recovered if the wool, before washing, be systematically lixiviated in a series of tanks by the aid of water at a temperature of about 45° C. in order to obtain a concentrated solution of the yolk. To this end the solution containing the highest percentage of yolk is employed for treating the fresh wool, whilst the nearly exhausted wool is treated with fresh water. In this manner a solution of about 10° B. is obtained, which can be converted into crude potash by concentration and calcination. According to Havrez, the concentrated extract may also be worked up into potassium ferrocyanide if treated with an addition of nitrogenous materials.

Scouring Wool by the Maertens Process.

Attempts have been made to replace the ordinary washing process by treating the raw wool with fat solvents such as carbon disulphide, benzine, carbon tetrachloride, etc., and this idea has been admirably developed in the Maertens process, with which the Société Solvant Belge at Verviers was able to wash 50 tons of wool per diem with a staff of only ten hands and four overlookers.

The process consists in treating the wool with a petroleum spirit (b.p. below 100° C.) in closed vessels for 20 minutes. The operation is conducted systematically, so that the unwashed wool comes first into contact with fat-laden solvent, and finally with fresh solvent, three extractions being sufficient. To lower the inflammability of the benzine the work is carried on in an atmosphere of carbon dioxide.

The final residue of benzine in the extraction apparatus is distilled with steam; and the cleaned wool is immersed in water, the adherent impurities becoming detached and settling to the bottom.

In this process, not only is the whole of the solvent recovered, but also the whole of the wool fat and in a relatively pure condition, the sale of this by-product nearly paying the working expenses of the entire plant.

Carbon tetrachloride has not proved suitable for wool washing, being easily decomposed and liberating hydrochloric acid which corrodes the apparatus; and no favourable result has attended the employment of carbon disulphide.

Washing Woollen Yarn.—Woollen yarns cannot be thoroughly purified unless the raw wool has been washed perfectly clean. All that the present operation has to effect is the removal of the oil added before spinning; and the method of treatment and composition of the washing liquor depend entirely on the degree to which the oil used is capable of saponification and emulsification. The yarn is treated in a solution of soap or soda (or both) at a temperature of about 40° C. until it ceases to feel greasy, which generally takes about half an hour. The wool is then rinsed in warm water, in order to prevent the residual fatty particles solidifying and sticking to the wool. It is therefore impossible to wash all yarns on a rigidly fixed plan, though generally a solution containing 1 per cent. of soap and 3 per cent. of soda, calculated on the weight of the yarn, will be strong enough. Worsted yarns are always washed with soap only.

A very useful method of cleaning fine wools is washing with ammonia; but this has not found any extensive application. The wool is first washed with ½ to 1 per cent. of soap and a little ammonia; then entered into a second weak ammonia bath, and rinsed. An addition of turkey-red oil, or Monopol soap to the baths is always advisable.

Washing Woollen Piece Goods. As in the case of yarns, woollen goods made from carded yarn are washed with soap and soda; worsteds with the former alone. The piece is thoroughly steeped with soap solution, or sodium carbonate solution 3 to 5 B., in the machine, and is left in soak for half to three-quarters of an hour, after which it is rinsed by adding fresh water until the effluent runs away clear. Should the goods still feel greasy, the operation is repeated.

Woollens are occasionally washed with soda alone, for the sake of cheapness, but this is inadvisable, as it makes the fibre harsh.

Worsteds are preferably washed twice, half an hour each time, in a 5 solution of olein (soft) soap.

The use of ammonia can also be highly recommended for washing piece goods.

Blueing or White Dyeing.

As already stated, the yellow tinge of imperfectly bleached fibres is often converted into a more or less pure white shade by the aid of blue dyes.

Cotton yarns, for example, are blued after bleaching by treating them with ultramarine in a soap bath, whilst cotton piece goods are treated with the same pigment in the dressing process.

White silk is blued in a lukewarm soap bath containing a very small quantity of some blue or violet dye, the various blue methyl violet marks being most frequently used for this purpose.

This blueing process is of far greater importance in the case of woollens intended for parti-coloured or fancy articles. In this case a wide range of white shades is required, and, as in the case of silk, is usually obtained with methyl violet blues in a lukewarm soap bath.

The chief difficulty in blueing resides in the accurate matching of the required tint. Of particular importance when methyl violet is employed is the amount of soap taken for the bath, since if an excess be used, an insufficient quantity of the dye will be absorbed, whilst in the contrary event the dyeing is liable to become irregular. The blued yarn has then to be sulphured, so that, in dyeing, the alteration sustained by the colour in this operation has also to be taken into consideration.

So-called "pure white" is best obtained by first blueing the goods very slightly in a hydrosulphite bath, and then shading off with fast acid violet, A2R (*Hochst*), which is a fast and readily distributable dye, in a fresh bath.

It is still customary in some places to dye woollens white by treating them with some insoluble alkaline earth salt, such as calcium carbonate, barium sulphate, etc., held in suspension in water; or by precipitating these substances direct on the fibre by passing the piece through a solution of sodium sulphate, and then immersing it in dissolved barium chloride.

Carbonising.

In addition to other impurities, sheep's wool contains burrs and other vegetable fragments, which adhere to the fleece and cannot be removed by washing. When such wool is dyed, the cellulose of the vegetable matter absorbs the dye less readily than the wool fibre, and then becomes apparent in the material as light-coloured spots or "nops". Formerly these were removed by cutting with a nopping tool, or hidden by staining with nop tinctures, but this procedure had many drawbacks, the cutters being liable to damage the cloth, whilst the staining was of a merely superficial character, and far from permanent.

At the present time this method has been superseded by carbonising, an operation whereby the vegetable matters in the wool are eliminated by the aid of acid and heat, which converts the cellulose into hydrocellulose, the latter being easily removed by mechanical means. The operation derives its name from the carbonised appearance assumed by the vegetable matter under the treatment applied.

The reagents employed are sulphuric and hydrochloric acids, the former in a free state, the latter in combination as aluminium chloride or magnesium chloride, both of which split up into oxychlorides and free hydrochloric acid when heated. (The statement that these chlorides are converted into oxides and hydrochloric acid at the temperature employed in the carbonising process is incorrect.)

The woollen material to be carbonised must be clean, and, in particular, free from fatty matter. If the wool contain any soap residue, the carbonising process fixes the fatty acids upon the fibre in such a manner that their subsequent removal by washing is well-nigh impossible, and they will then show up as patches when the wool is dyed.

Carbonising is applied only to loose wool or piece goods; and even the latter alternative is attended with numerous drawbacks, owing to the formation of acid spots, soda spots, and other spots arising from impurities in the goods, these defects for the most part only becoming visible after the material has been dyed. On the other hand, these inconveniences are practically non-existent when the wool is carbonised loose, and for this reason the practice of carbonising in the piece has been discontinued at Verviers and many other places. Where still in vogue the process is applied to piece goods at various stages of manufacture, either just before or just after milling, or after dyeing. This refers only to woollens, worsted fabrics being seldom carbonised at all, since if not more than ten nops are found in a hundred-yard piece they are taken out by means of a nopping tool, and carbonisation is therefore superfluous.

The process is divided into three principal stages: impregnating the material with the carbonising reagent; the actual carbonising; and the removal of the residual reagent.

Impregnation consists in steeping the material for several hours in the reagent. In the case of sulphuric acid, the operation is performed in lead-lined tanks. To ensure thorough impregnation, piece goods must be drawn through the steeping liquor, the excess of the latter being squeezed out by means of rollers and removed by the hydro-extractor (which for this purpose must be lined with coarse cloth to prevent contact with the metal). They are then dried at a gentle heat, generally in a moderately heated drying chamber; though sometimes this preliminary drying is omitted, and the goods are carbonised in their wet state. In such event, however, it must not be forgotten that the action of the reagent is far more energetic.

Care is necessary to see that the impregnation is performed in a perfectly uniform manner, and that no irregularity occurs in the drying, and consequently in the distribution of the carbonising reagent, since this will certainly result in the production of spots in dyeing. This is especially the case in carbonising piece goods, and the latter should therefore be carefully drained in the hydro-extractor and carbonised as soon as possible, being stored in the meantime away from contact with light and air.

The actual carbonising is effected by passing the impregnated material through a carbonising stove, such as the one illustrated in Figs. 21 and 22.

Fig. 21 represents a wool-drying stove also used for carbonising. The wool is introduced at *a*, and passes through the chamber *b*, falling from one set of conveyers to the others in succession until it is discharged at *c* into the box *d*.

Mostly there are only two superimposed or juxtaposed chambers: one in which the wool is pre-dried at a low temperature, and the other in which the material is carbonised at a high temperature. Ventilators are provided for the escape of the moist air, and the chamber is heated by means of gilledas light-coloured spots or "nops". Formerly these were removed by cutting with a nopping tool, or hidden by staining with nop tinctures, but this procedure had many drawbacks, the cutters being liable to damage the cloth, whilst the staining was of a merely superficial character, and far from permanent.

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All these apparatus can also be used for drying wool.

Piece goods are carbonised in similar apparatus,[1] the pieces being led over rollers up and down through the chamber. Heat is imparted by iron steam-pipes led through the chamber, but in order to prevent rust spots, all the pipe connections must be situated outside the chamber.

The temperature and the duration of the process depend on the reagent, and, to a smaller extent, on the quantity of impurities to be eliminated, as well as on the thickness of the material in the case of piece goods. Full particulars will be found below in dealing with the various reagents used.

After carbonising, the loose wool is willowed—piece goods being beaten—at once to remove the burrs, etc., whilst still dry and brittle.

Finally, the residual reagent must be got rid of. When magnesium or aluminium-chloride has been used, this is effected by treatment with ½° to 1° B. sulphuric acid, followed by neutralising with weak alkali and washing in water, but in the case of sulphuric acid the excess has to be neutralised by treating the wool with a lukewarm solution of soda (about 2° B.) for half an hour or an hour. The elimination of the acid must be complete, since any allowed to remain would concentrate in the subsequent drying, and corrode the wool fibres, the result being the production of acid stains in dyeing. However, when the goods are to be dyed with acid dyes the neutralisation may be omitted, the removal of the acid being then unnecessary. This happens, for instance, in the dyeing of fezzes.

After neutralisation is finished the soda in turn must be thoroughly got rid of by washing, since otherwise the concentration of the alkali in drying would result in the formation of soda spots on the dyed goods being subsequently exposed to a high temperature (as in the dressing process).

At Verviers and other places the neutralising operation is performed with soap and soda in small (three-tank) leviathans, the soap being used for correcting the harshness produced in the fibre by carbonising.

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[1] Made by Haubold, R. Kühne, etc.

Carbonising Agents.—The most important and most largely used of these is sulphuric acid, which is only replaced by magnesium- or aluminium-chloride, when the operation has to be performed on woollen fabrics dyed with colours unable to resist the acid; otherwise dyed cloth can be carbonised with this acid. Both the above-named chlorides are milder in their action than the acid in question, and have less effect on the fibre or colour of the material under treatment. This is due to several causes. In the first place, sulphuric acid is a stronger acid than hydrochloric acid, the more so that it is not volatile at the temperature of the carbonising process, and therefore remains in the fabric. Secondly, in using the said chlorides, the temperature is such that ammonia is liberated from the wool and neutralises the freed hydrochloric acid to some extent, so that the latter only exerts its full power in such places where vegetable matters occur. Finally, the action of the hydrochloric acid is weakened by the oxychlorides formed.

The main defect of the chloride process of carbonisation resides in the high temperature required for the decomposition of the reagents, the consequence being that, especially with magnesium chloride, the wool is always faintly tinged with yellow, thus impairing the purity of the more delicate colours, especially blues. This defect is less apparent with aluminium chloride, this salt nevertheless being ever less and less used, on account of its higher price. Generally speaking, therefore, only two carbonising agents—sulphuric acid and magnesium chloride—are in current use.

Carbonising with Sulphuric Acid.—The usual procedure is to employ 3½ to 4° B. acid, the temperature of the operation being 80° C., and the duration about twenty minutes. The practice, however, varies in different establishments, the concentration ranging from 2 to 6° B. The more dilute the acid the higher the temperature required, and *vice versâ*. Thus, acid of 2° B. strength must be applied at a temperature of about 100° C., whereas 6° B. acid can be used at about 60° C. It is always preferable to work with weaker acid and employ a higher temperature than under converse conditions.

Where the fabric to be carbonised has cotton selvedges, the latter must be protected from attack by coating them over with a solution of soda, thickened with fuller's earth and gum. This practice may, however, prove a source of inconvenience, inasmuch as by using an excess of the said solution the wool bordering the selvedges is liable to corrosion from the soda, and soda spots will form in dyeing. The defect may be obviated by using sodium acetate instead of soda.

Carbonising with Magnesium Chloride (A. Frank, 1877). —The fabric is impregnated with a 15° B. (or weaker) solution of magnesium chloride, and carbonised for thirty to forty-five minutes, at 140° to 150° C. According, however, to Breinl and Hanofsky a 9° B. solution is strong enough.

If magnesium chloride be heated by itself to 140° to 150° C. for some time, only about one-half of the contained chlorine will be liberated as hydrochloric acid, an oxychloride with a strongly alkaline reaction being left; and the same result apparently ensues when a fabric is carbonised with this salt. Accordingly, the fabric so treated gives a strongly alkaline reaction afterwards, and this reaction may be occasionally so pronounced that the fibre is attacked, and assumes under the microscope the same appearance as when corroded by soda (see Fig. 12). To prevent this, it is necessary to dry the material thoroughly after impregnation and to keep the carbonising chamber perfectly dry. From the foregoing, it also follows that dye-stuffs sensitive to the action of alkalis will suffer more or less when carbonised with magnesium chloride. For the most part, however, the defect can be corrected by after-treatment with dilute acid.

When the piece to be carbonised is one with cotton selvedges, the latter must not be coated over with soda, since the resulting alkaline magnesium carbonate would corrode the wool. Consequently, in such event, the carbonising must be performed with sulphuric acid; or the selvedges could be dressed with sodium acetate.

In carbonising with magnesium chloride, care must be taken that no magnesia soaps are formed in the material, since these render the fibre harsh and cannot be removed by washing.

Carbonising with Aluminium Chloride (R. Joly, 1874).—The fabric is steeped in a 7° B. solution of aluminium chloride (as neutral as possible), then well dried, carbonised at 120 to 130 C. for one hour, and well washed.

When aluminium chloride is heated by itself at 120° C., about four-fifths of its chlorine is driven off as hydrochloric acid. Here, also, an oxychloride is formed, which, however, differs from that of magnesium by having an acid reaction.

As in the case of magnesium chloride, care should be taken to prevent the formation of a soap of the metal on the fabric, and, finally, it may be mentioned that a variety of carbonisation effects may be produced on mixed cotton and wool fabrics by printing with aluminium chloride. Owing, however, to the cost of this reagent and its lack of advantages, its use in carbonising is now practically abandoned.

Carbonising with free hydrochloric acid was practised, but only for a short time, in Belgium. The hydrochloric acid gas, produced by the action of sulphuric acid on common salt in retorts, was conducted by means of a current of air over the wool spread out on frames, or a solution of the acid was sprayed over the wool by a revolving brush, the material being afterwards exposed to a high temperature. The disadvantages of the method consisted in the corrosion of all the metallic fittings of the apparatus, and in the difficulty experienced in regulating the strength of the reagent.

Nevertheless, this method is frequently used for carbonising shoddy and similar goods, the materials being treated with hydrochloric acid gas in revolving drums, or else left to soak for some time in hot dilute hydrochloric acid, in wooden vats.

Of late years, sodium bisulphate has been advocated for carbonising wool. The strength of the solution is 5° to 6° B., and the operation takes about three-quarters of an hour at a temperature of 100° C. The effect is, however, less powerful than sulphuric acid; but, on the other hand, there is not the same attack on the wool, and the method is quite suitable for application in numerous instances. The goods are finally neutralised with a 2 to 3° B. solution of sodium carbonate.

The defects of manufacture liable to be produced by the operation of carbonising are, as already mentioned, the stains developed in the subsequent dyeing, which are due to either acid or alkali.

Soda stains may result from neutralisation or from carelessness in carbonising with magnesium chloride, or, finally, from dressing the cotton selvedges with soda. They frequently appear as dark patches in the dyed cloth, and can almost invariably be recognised by microscopical examination.

Acid stains occur solely after carbonisation with sulphuric acid, and show up as light patches in the dyed cloth (sometimes also before dyeing). If the action of the acid in these places has been strong, they will be found to damp more readily in water than the other parts of the material. These stains require a very experienced eye to detect under the microscope.

However great the care bestowed on the sulphuric acid carbonisation process, the presence of impurities is liable to cause acid stains; hence, in the case of such wools, it is better to carbonise with magnesium chloride.

CHAPTER III.

MORDANTS AND MORDANTING.

Mordants.

IN the operations of dyeing and printing fabrics a number of metallic salts are employed to fix the mordant dyes, in the form of lakes, on the fibre. The lakes are compounds of the dye-stuffs with metallic hydroxides. They are insoluble and very resistant towards reagents, and the usual method of bringing them on the fibre is to first precipitate the hydroxide, from a metallic salt, on the fibre and then dye with a suitable dye-stuff. The metallic salts, or hydroxides, used for this purpose are termed "mordants," and the operation of precipitating the hydroxides in and upon the fibre is known as "mordanting".

To be of practical utility, a mordant must fulfil the following requirements. Cheapness; easy precipitation of the hydroxide; insolubility in water on the part of the hydroxide, coupled with a certain affinity for the fibre; the resulting colour lakes must be of good colour and as "fast" as possible, *i.e.* capable of withstanding the influence of light, acids, alkalis, etc. These conditions, however, are fulfilled by only comparatively few metallic salts, and, in fact, the only mordants in practical use are the alumina, iron, chrome, tin, and copper mordants. The alkalis are not mordants, both their hydroxides and the compounds of these with dye-stuffs being soluble in water, and though the alkaline earths give insoluble colour lakes, the colour of these is poor, and they have no affinity for the fibres. As regards the remaining metals, not all of these have been examined as to their capacity for forming lakes. Some of them furnish good colour lakes, which, however, are too dear for practical application (*e.g.* nickel), whilst others, though cheap, give lakes deficient in stability (*e.g.* zinc).

Nevertheless, in certain special instances, *e.g.* for alizarine blue in calico printing, these metals also are used as mordants. It should, however, be mentioned that certain dye-stuffs, *e.g.* alizarine red S, alizarine-cyanine 2G, and others, give handsomer lakes with zinc than with the more frequently used chrome mordants.

The suitability of a large number of metals to act as mordants for cotton was investigated by A. Scheurer, who found that several of them, especially thorium, yttrium, zirconium and beryllium are dyed more readily by many dye-stuffs than are the mordants in general use.

According to Dreher, titanium, in the form of titanic acid - $Ti(OH)_4$ - forms a suitable mordant for leather, because it can be fixed in the cold. The Korichrom of commerce is a titanium lactate mordant.

Without going more deeply into the constitution of the colour lakes, it may be mentioned that for many really fast lakes, lime is a necessary constituent, as well as the mordant, and that even such lakes that can be used without containing lime are all the easier made and faster to acid when lime is present. In the complete absence of lime, alizarine cannot combine with alumina at all, since a fabric that is devoid of lime and is mordanted with a pure alumina preparation, gives only a yellowish and quite unstable dyeing with alizarine. Again, whilst faintly alkaline bodies like sodium acetate will assist the combination of alizarine with an alumina mordant in the dye bath, the resulting colours will not stand acid. The fast alizarine red dyeings therefore consist, not of an alumina lake of alizarine, but of an alumina-lime lake; and therefore lime salts may be termed auxiliary mordants.

One and the same dye-stuff will furnish colour lakes of divergent shade and fastness with different mordants. The lightest and brightest are the tin and alumina lakes, the copper and iron lakes being the darkest, whilst the chrome lakes occupy an intermediate position in this respect. In point of stability, it is a difficult matter to generalise, but, as a rule, the copper and iron colour lakes are the fastest under the influence of light.

Of considerable practical importance is the still insufficiently appreciated circumstance that, in many instances, a dyeing that will stand milling much better can be obtained by using several mordants in conjunction than if they were employed separately (see Alizarine red on wool).

The behaviour of the various textile fibres towards mordants is mainly dependent on their nature, and, in a secondary degree, on the metallic salt of which the mordant is composed. A general description of the behaviour of the fibres towards mordants, and the operation of mordanting, will therefore be given first, after which the special applications of the separate mordants will be briefly considered.

Mordanting Wool.

If wool be treated in a cold solution containing a small quantity of a mordant, a portion of the metallic hydroxide will be taken up by the wool, the other part remaining in solution. At the same time a small proportion of the acid of the mordanting bath is also taken up by the fibre. On repeating the experiment in more concentrated solutions, it is found that the stronger the bath the higher the ratio of absorbed acid to absorbed base. Wool therefore possesses an adsorbent capacity for both bases and acids, each of the two constituents of the salt used being taken up independently and as though it alone were present in the mordanting liquor. The possibility of this is afforded by the circumstance that the metallic salts used as mordants undergo more or less extensive hydrolytic dissociation in aqueous solution more rapidly in the warm and best in the neighbourhood of boiling temperature.

From the foregoing it is evident that dilute solutions are necessary in the practical performance of the mordanting process, the object of the operation being solely to deposit a metallic hydroxide on the fibre; whilst the amount of acid absorbed should be as small as possible, owing to its unfavourable influence on the formation of a lake and on the shade of the colour in the subsequent operation of dyeing.

Consequently, mordanting should be effected hot and not in the cold.

It has also been noticed that in the event of too rapid absorption the hydroxide is generally fixed in an imperfect manner, being more superficial and often causing uneven dyeing. The mordanting should therefore be carried on slowly and gradually, on which account salts that are easily dissociated, like the acetates and basic salts, cannot be used for mordanting wool. The most suitable mordants are—of the alumina mordants, alum and aluminium sulphate; of the iron mordants, ferrous sulphate; of the copper mordants, copper sulphate (blue vitriol); of the tin mordants, stannous chloride (tin salt); and of the chrome mordants, potassium and sodium bichromates, and chromium fluoride. Even when these are used the operation will go on too fast if the wool be immersed in the boiling hot mordant liquor; and the process must therefore be pursued in the following manner: The wool is first thoroughly wetted by boiling in water for half an hour to one hour, after which it is entered in the bath of lukewarm mordant, to which a small quantity of an acid substance has been added (see below). The temperature of the bath is then slowly raised to 100° C. (in about an hour) and boiling is continued for an hour to an hour and a half longer. Loose wool and yarn must be thoroughly worked about in the bath to ensure uniform mordanting of the whole of the fibre, and piece goods are kept in motion by winding.

After mordanting, the goods are generally merely cooled down and the excess of liquid removed, rinsing being omitted. Loose wool is spread on the floor, yarn being unwound and hung up, and piece goods alternately folded and opened out again, and finally hung on a wooden frame to allow the excess of bath liquor to drain away. The hydro-extractor is, however, a better means of draining the goods.

Before drying, the mordanted wool must be dyed, since otherwise it would have to be re-wetted for dyeing—a difficult operation when alumina mordants have been used. The usual custom is to leave the wool overnight after mordanting, the reason given for this procedure being, that unless allowed to stand for some time the wool takes more dye-stuff to dye it than otherwise. The real purpose of the delay, however, is apparently to give the excess of mordant time to drain off, since the larger the amount of this liquor introduced into the dye bath the greater the loss of dye through useless precipitation as insoluble colour lake. It is therefore more rational to wash the mordanted woollen material previous to dyeing, but it should first be allowed to get quite cold, or part of the fixed mordant will be sure to wash out.

When the wool has been mordanted with a sulphate, *e.g.* alum or ferrous sulphate, it will always contain a little sulphuric acid; whereas when stannous chloride has been used the fibre takes up only a very little hydrochloric acid, if any at all, partly because the amount of this mordant used is small, and also because wool has probably a smaller capacity for absorbing hydrochloric acid than it has for sulphuric acid. Should the acid so absorbed be found to have an unfavourable effect on the dye, the defect may be remedied by adding a little ammonia, to neutralise the acid, towards the end of the dyeing process. This is frequently done in dyeing with logwood, and the same effect may be produced by means of calcium acetate (obtained by correcting the water with acetic acid), the favourable influence of which salt in logwood dyeing is thus explained.

In the foregoing method of mordanting, it is always customary to add a small quantity of some acid substance to the bath, such as potassium bitartrate, oxalic acid, or sulphuric acid, the first named being most frequently used, notwithstanding its high price. The part played by these adjuncts has not yet been elucidated; but it is assumed that in mordanting with sulphates, chlorides, etc., they retard the dissociation of the salts in question and protract the absorption of the hydroxides by the fibre. In ordinary mordanting with potassium bichromate these acid substances play a different part, as will be set forth in the description of the process later on.

When dyeing with hard water and using bitartrate, it will be necessary to correct the water beforehand by an addition of 5 to 10 per cent. of 8 B. acetic acid, since otherwise the bitartrate would be neutralised by the lime in the water, and would cease to act.

Mordanting Silk.

Silk has a high capacity for adsorbing the most divergent substances of acid and basic character, though this property is manifested in a different manner to that of wool, being greater in the cold and at medium temperatures than at boiling heat; consequently, if an attempt be made to mordant silk in the same manner as wool, only a very small quantity of the hydroxide will be taken up. The most suitable mordants for silk are cold concentrated solutions of basic salts, readily dissociated by dilution with water. On prolonged immersion in such solutions the silk takes up a portion of the hydroxide and a part of the acid present—just as in the case of wool. On then washing the material in water, the unfixed excess of the mordant is removed, on the one hand, whilst, on the other hand, a part of the same is dissociated by the dilution, and a further amount of the hydroxide is fixed on the fibre. To complete the fixation the silk is finally entered in an alkaline bath, which removes the last traces of acid present, before washing. The operation of washing between the mordanting and the fixing processes is performed with a large volume of (preferably running) water, a special washing apparatus being used, consisting of a series of hollow, perforated porcelain cylinders. These are set parallel, side by side, and are caused to revolve after the silk hanks have been hung upon them. By means of water discharged through the perforations and through jets placed between the hanks, the material receives a thorough washing.

It will be readily understood that hard water is advantageous for this purpose.

The best mordants for silk are basic alum, aluminium acetate, basic ferrous sulphate ("Rouil mordant"), basic chromium chloride, chrome mordant GA III, and stannous chloride.

Mordanting Cotton.

Cotton differs from wool and silk in having practically no adsorptive capacity for metallic hydroxides, and must therefore be mordanted in a different manner. There are two ways of doing this. In one the metallic hydroxide is deposited in and upon the fibre by first impregnating the latter with acetic acid, the bulk of which is then volatilised by drying and the remainder eliminated by treatment in an alkaline bath. In the other method the hydroxides are precipitated on the fibre as insoluble tannates or fatty-acid salts by first steeping the cotton with tannic acid or fatty acid, and then treating it with the metallic salt used as the mordant.

The former method is used exclusively in dyeing piece goods, being difficult to perform with regularity in the case of yarns. Moreover, it is restricted to mordanting with alumina and iron. The *modus operandi* is as follows: The cottons are first impregnated in a thoroughly uniform manner, with a dilute solution of aluminium acetate or iron pyrolignite in a padding-machine, the operation being termed "padding."

In the padding-machine sketched in Fig. 22 the goods are unwound from the roller *a* and passed over the stretcher *b* to the trough *c*, which contains the mordant and three guide rollers *d*; thence the piece passes between the wringer rollers *e*, *f*, and is finally wound on the roller *g*. All the rollers are of wood, and their trunnions rest on sloping arms *h*, so that the roller *g*, which is driven by the upper wringer roller, can move slowly upwards in proportion as its diameter increases in consequence of the cloth being wound upon it. The upper wringer is weighted by the weight *m*, which acts through the levers *i*, *l*, and the rod *k*, the length of the latter being adjustable by turning the extension screw *n*.

With light goods a single passage through the padding-machine is sufficient, but heavy goods require to be put through twice. This done, the piece, instead of being wound on the roller *g*, as shown in the figure, is led (over as few guide rollers as possible) up and down through a gently heated chamber, known as the "hot flue," where it is dried sufficiently to make it fit for transport. In this manner the cotton retains the mordant acetate in an almost entirely unaltered condition. The amount depends on the concentration and on the pressure exerted by the wringers, this being usually adjusted so that the goods retain about their own weight of mordant solution. The next stage is to hang the goods in a warm chamber, extending through several storeys in the building and heated by steam pipes laid on the floor, covered by a layer of spars. A second set of heaters is preferably arranged above the ceiling, to prevent the goods being spotted by condensed moisture. In addition to a high temperature, a certain degree of moisture in the atmosphere is necessary to the due performance of this process, for which purpose water vapour is introduced into the chamber by allowing drops of water to trickle on to the heating-pipes from perforated pipes mounted just over the latter.

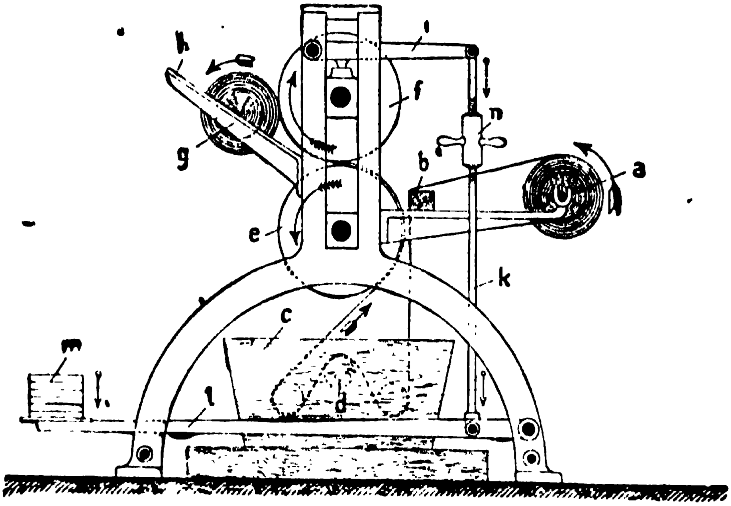

FIG. 22.

The degree of moisture is registered by a suitable hygrometer. Ventilation is provided by means of air-pipes reaching from the floor up to above the level of the roof. The printed goods are hung in this chamber for about forty-eight hours, at a temperature of about 30° C., the wet bulb of the thermometer indicating some 3° to 4° lower.

This operation is often styled the "oxidation process," probably because it is frequently employed for developing aniline black, in which case oxidation actually occurs. When the goods have been mordanted with acetate, the acetic acid is volatilised in the hot chamber, leaving the metallic hydroxide deposited on the fibre in the finely divided state necessary for the subsequent dyeing. When iron is used, a gradual oxidation to ferric hydroxide also occurs. It is essential that this process should be carried on in a very gradual manner, since, if the hydroxide be fixed rapidly—for example, by steaming for a short time—the colours will come out less full and handsome in dyeing.

To thoroughly fix the hydroxide, the residual traces of acid must be removed by a mild alkali, for which purpose the goods are next "dunged" by passing them over guide-rollers through several vats—at least two—containing a decoction of cow dung and levigated chalk (see Fig. 23). This decoction is prepared

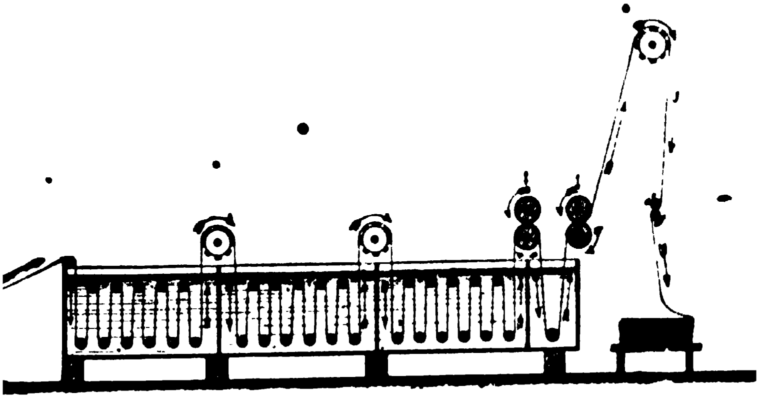

FIG. 23.

by boiling 4 parts by weight of cow dung and 0·3 part of levigated chalk in 7 parts of water for about two hours. The first vat is charged with 8 cwt., and the second with 6 cwt. of the preparation, the temperature being maintained at 60 and 50° C. respectively. When about 600 yards of material have been passed through the vats, the baths are replenished with about 30 lb. of the preparation. The goods remain in the bath for about two minutes.

The levigated chalk and the faintly alkaline substances present in the cow dung neutralise the residual traces of acid in the material.

Many attempts have been made to replace cow dung by faintly alkaline salts, such as ammonium carbonate, sodium phosphate, arsenite, silicate, etc., but though these all act in the desired direction the best colours are still obtained by the use of cow dung. This may probably be attributable to the mucinous condition imparted to the water by the substances dissolved out of the dung, in consequence of which no scouring action is exerted on the goods during their passage through the bath. The best substitute for cow dung out of those named above is ammonium carbonate, employed in the state of a 2 per cent. solution, and at ordinary temperature.

The mordanting process is completed by swilling off the impurities collecting on the fibre in the dung bath, and by a thorough washing.

Similar in principle, but less objectionable in performance, is the mordanting of cottons with chromium bisulphite or chromium acetate, the goods being padded with the dissolved mordant, and fixed with boiling hot soda solution after drying.

Mordanting with the assistance of tannic acid or fatty acids will be described later on in dealing with these fixing agents.

The mordants used in practice are salts of aluminium, iron, chromium, tin, or copper. The two last named are the least important, the principal mordants now used being those of the chromium group.

Alumina Mordants. These are employed in the production of the following colours: Alizarine red and alizarine orange, on all three classes of fibre; alizarine rose-red on cotton; amethyst, with cochineal, on wool; yellow shades with natural dye-stuffs; logwood blue on wool; and certain mixed shades, with alizarine and other dye-stuffs, on cottons.

In most cases the alumina mordants should be free from iron, the iron lakes being darker and duller in colour than the alumina lakes, so that, if present, even a small amount of iron would suffice to dull the colours produced by the aid of alumina mordants. For instance, alizarine gives a brilliant red with alumina mordant, but a dull violet lake with iron; consequently, a handsome alizarine red can only be developed when iron is absent. According to the researches of Lunge and Keler, the aluminium sulphate used for dyeing alizarine red should not contain more than 0·001 per cent. of Fe. For the preparation of a 6° B. aluminium acetate for alizarine steam red, the aluminium sulphate may contain up to 0·005 per cent. of Fe without any ill-effect on the colour.

The most important salt of alumina is alum ($Al_2(SO_4)_3K_2SO_4$ $24H_2O$), which is used both *per se* and in the preparation of other alumina mordants. Its active constituent is aluminium sulphate, the potassium sulphate playing no important part. Hence aluminium sulphate can also be used as a mordant, and, indeed, is preferable, inasmuch as it can now be obtained at a relatively lower rate, in comparison with the percentage content of alumina present, than alum. The latter continues to be used, however, in many places, its crystalline form being considered to afford a better guarantee of purity. Nevertheless, the commercial sulphate in lumps is also, for the most part, free from iron, but, its composition being irregular, needs checking by analysis.

Alum and aluminium sulphate are the only alumina mordants used for wool. The quantity of alum taken varies from 6 to 12 per cent., according to the nature and intensity of the dyeing, and it is employed in conjunction with 2 to 5 per cent. of potassium bitartrate or oxalic acid and a 30 to 40-fold quantity of water; the above percentages being calculated to the weight of wool under treatment.

Alum, as such, is unsuitable for mordanting silk and cotton, its sulphuric acid preventing the fixation of the hydroxide, unless previously neutralised, to some extent, by an alkali. A partly neutralised alum solution of this kind is known in practice under the name "basic alum," the assumption being that it contains a basic salt of alumina. Thus, for example, if one molecule of sodium bicarbonate be taken to neutralise the sulphuric acid in one molecule of alum, the reaction ensuing may be expressed by the following equation:—

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Al_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2.$$

Here, as in other cases where a basic salt is formed in an analogous manner, the formula deduced for the resulting salt from the equation is hypothetical only, and expresses the degree of neutralisation produced by the alkali.

With regard to the production and behaviour of these basic salts in general, and not merely those of alumina, the following observations may be made: In their preparation, the dissolved alkali—generally soda—is added by degrees to the solution of the salt to be rendered basic, and kept stirred, any resulting precipitate being redissolved by warming. This, however, is not always possible. The more strongly basic the mordant, the more readily does it undergo dissociation into the corresponding hydroxide or allied insoluble salt. This dissociation is accelerated by heat and dilution. Both the different mordants and the various salts of one and the same metal behave in a very divergent manner under this treatment; moreover, the capacity for dissociation of basic salts is appreciably influenced by the presence of extraneous salts. Thus, for instance, the neutralising of the acid in aluminium sulphate can be pushed so far, in the presence of certain salts (*e.g.* magnesium sulphate), that the composition approximates to $Al_2SO_4(OH)_4$, without causing precipitation. The precipitate obtained from alum solution by sodium carbonate has about the formula $Al_2(OH)_5(SO_4)_{\frac{1}{2}}$ and forms the ordinary gelatinous alumina of commerce.

The alumina mordant for silk is prepared (according to the prescription of the Badische Anilin & Sodafabrik) with a solution containing 60 grms. of alum and 6 grms. of soda crystals per litre.[1] After the addition of the alkali to the alum solution the liquid is warmed until the resulting precipitate has redissolved, whereupon the silk is entered in the bath, worked about for ten to fifteen minutes, and left in soak for at least twelve hours. It is then well wrung or drained in the hydro-extractor and entered in a bath of $\frac{1}{2}$° B. sodium silicate, worked about for a quarter of an hour, and carefully washed. The silicate treatment causes the deposition of aluminium hydroxide, and not aluminium silicate, on the fibre.

For mordanting cotton with alum, concentrated solutions are used, containing 100 to 200 grms. of aluminium sulphate per litre (10 to 20 per cent.), and are neutralised as far as possible with soda. Further particulars on this point will be given in treating of the fixing agents (fatty acids).

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[1] These proportions correspond to one molecule of sodium carbonate per three molecules of alum, and the resulting alumina salt will have the formula $Al_6(SO_4)_8(OH)_2$. In making calculations of this kind, the water of crystallisation in the different substances must not be forgotten.

Aluminium acetate is prepared by dissolving aluminium hydroxide in acetic acid or by decomposing alum or aluminium sulphate with lead acetate. When three molecules of lead acetate are taken to one molecule of aluminium sulphate, normal aluminium acetate is produced

$$Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 = Al_2(C_2H_3O_2)_6 + 3PbSO_4,$$

but on lowering the proportion of lead acetate sulphacetates are formed-

$$Al_2(SO_4)_3 + 2Pb(C_2H_3O_2)_2 = Al_2SO_4(C_2H_3O_2)_4 + 2PbSO_4.$$

For use as a mordant, it is unnecessary that the whole of the sulphuric acid present in aluminium sulphate should be thrown down; in fact, it is preferable in practice to select the proportions in the preparation of aluminium acetate so that a sulphacetate is produced instead of the normal acetate. Generally not more than a half to three-quarters of the total sulphuric acid is removed.

For use in calico-printing these mordant solutions are made as highly concentrated as possible, one method adopted being to dissolve the one salt and add the other in the condition of powder. For example, a 15° B. mordant can be obtained by dissolving 1 part by weight of aluminium sulphate and 1 part of lead acetate in 2 parts of water, this solution being diluted according to requirements, and occasionally rendered basic by an addition of chalk.

The various acetates may be diluted with water without undergoing dissociation; a few of them throw down a deposit when heated, but this is redissolved on cooling.

The aluminium acetate mordants are chiefly used in calico-printing, and also in piece dyeing cottons. For turkey-red dyeing, solutions of 2° to 3° B. strength are used.

Silk can be mordanted with 6° B. aluminium acetate just as well as with basic alum.

In the case of wool these salts are not used as mordants, but are employed as waterproofing substances in the dressing process.

For dull colours the pure salt is replaced by the cheaper aluminium pyrolignite.

Aluminium sulphocyanide is prepared, by double decomposition, from alum or aluminium sulphate and barium or calcium sulphocyanide

$$Al_2(SO_4)_3 + 3Ba(CNS)_2 = 3BaSO_4 + Al_2(CNS)_6.$$

It is used to replace aluminium acetate for alizarine steam red in calico-printing, since it does not corrode the steel doctors of the printing machine and does not introduce iron into the printing colours. As, however, it readily corrodes cotton fibre when hot, the printed goods must be hung some time previous to steaming. The salt has no other uses.

Sodium aluminate ($NaO . AlO$) is prepared by dissolving aluminium hydroxide in caustic soda and neutralising the excess of the latter. On account of its strongly alkaline reaction, this mordant can only be used for cotton, for which purpose it has several advantages over the other aluminium mordants. For instance, an alizarine red developed by its aid is less susceptible to the influence of iron and heat, and is easier to discharge. In mordanting cotton, the pieces are impregnated with a solution of sodium aluminate, dried, and passed through a warm solution of ammonium chloride (sal ammoniac), whereby aluminium hydroxide is precipitated on the fibre. It is used for turkey-red in the Schlieper and Baum method—though then fixed in a different manner—and also as an adjunct to naphthol preparations for nitraniline red, as well as being employed as a reserve under aniline black.

Aluminium fluoride forms a good mordant for wool, the colours being brighter than with alum; it is not used, however, in practice.

Of the other salts of alumina only the nitrate, chloride, and chlorate need be mentioned. These are used in calico-printing, the nitrate sometimes for alizarine steam red, the other two for red discharge on vat blue with alizarine. Aluminium chloride is also used in carbonising (*q.v.*).

Iron Mordants.—These play a most important part in black dyeing all three fibres with logwood; they are also used for dyeing wool brown with dye-woods, and on cotton for catechu and several alizarine dyes, for alizarine violet in calico-printing, for green with nitroso dyes, for Berlin-blue and chamois on cotton, and for darkening sundry tannin dyeings. The salts used as mordants are ferrous sulphate (green vitriol), iron pyrolignite, and so-called iron nitrate.

Ferrous sulphate and "Salzburg vitriol" (a mixture of ferrous sulphate and copper sulphate) are the only iron compounds used for mordanting wool. When the dyeing is for logwood black, a preliminary mordanting is given, in other cases the darkening method is practised. (See Dyeing.)

On cotton, ferrous sulphate is fixed on the fibre by means of tannic acid (*q.v.*); it is no longer in use for silk, except sometimes for black.

Finally this salt is also used as a reducing agent in the so-called vitriol vat.

Iron pyrolignite is prepared by dissolving scrap iron in crude pyroligneous acid, and forms the most important and almost the sole iron mordant for calico-printing. In cotton-dyeing it is used according to the two methods already described, the solution employed for dark colours being only a few degrees B. in strength.

The chief constituent of iron pyrolignite is ferrous acetate, which, however, in the pure state is not a good mordant for cotton, being too readily oxidisable, and consequently poorly fixed on the fibre. The pyrolignite, on the other hand, forms a good mordant owing to the presence of other matters which retard the oxidation of the acetate. With the same object, and also to retard the fixation of the hydroxide, it is customary to add a solution of arsenic in acetic acid. Sometimes, however, *e.g.* for pale chamois (and also for alizarine violet), pure ferrous acetate, prepared from ferrous sulphate and lead acetate, is employed; this product frequently contains an excess of lead acetate, which then comes down as lead hydroxide with the iron chamois and lightens the shade.

When iron pyrolignite is used for mordanting piece cottons along with aluminium acetate, the latter should be as free as possible from sulphuric acid, since otherwise ferrous sulphate will be formed, and this is difficult to fix. In silk-dyeing, the pyrolignite is used for black, and is fixed with tannic acid (*q.v.*). For wool, it is used only in the case of pelts, etc., that are mordanted cold.

Iron nitrate is the name given to a class of mordants produced by the action of nitric and sulphuric acids in variable quantities on ferrous sulphate, and consisting of a mixture of neutral and basic ferric sulphates and ferric nitro-sulphates.

The following proportions of the said reagents are used in the preparation of normal ferric sulphate:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

By using less sulphuric acid, *e.g.* only half the above quantity, a basic ferric sulphate is obtained—

$$12FeSO_4 + 3H_2SO_4 + 4HNO_3 = 3Fe_4(SO_4)_5(OH)_2 + 4NO + 4H_2O.$$

By employing more nitric acid, nitro-sulphates are produced.

In reality these mordants do not contain any nitrates, and the term by which they are known is therefore inaccurate. They are put on the market in the form of reddish-brown concentrated solutions, frequently containing free nitric acid.

The fixation of these mordants on the cotton fibre is effected by the aid of tannic acid, as in the case of iron pyrolignite. Their principal application is in the black dyeing of silk, for which purpose a mordant is prepared, the composition of which nearly corresponds to the formula in the above equation, *viz.* $Fe_4(SO_4)_5(OH)_2$, and which is known as "Rouil mordant". The method of use differs according as the silk is in the raw, souple, or scoured state. The last named is mordanted in the following manner:—

The silk is immersed in a 30° B. solution of the mordant for about an hour, after which it is taken out, unwound, and carefully washed, preferably in hard running water.

These operations are usually repeated several times over, the final fixation of the mordant being effected in a boiling hot soap bath. The mordanted silk must not be allowed to dry, or it will be corroded by the mordant. Raw and souple silk are mordanted in a weaker solution, and, for the sake of cheapness, the fixing is generally performed with soda instead of soap.

Chrome Mordants. At the present time the chrome mordants are the most important in use, many dyeings formerly mordanted with alumina or iron salts being now treated with chrome salts instead, and, with the exception of a few of the alizarine dyes, all artificial mordant dye-stuffs are fixed with chrome mordants exclusively. Their chief use is in the fast dyeing of wool.

These mordants differ greatly in behaviour from the iron and alumina mordants, being, on the one hand, more difficult of dissociation, and therefore harder to fix on the fibre, whilst, on the other hand, the combination of the fixed chromium hydroxide *i.e.* the formation of the colour lake is effected more readily. As regards the first-named property, this comes in evidence already during the treatment of the solution with alkaline substances, the quantitative precipitation of the hydroxide generally requiring the temperature of boiling-heat for its accomplishment, a property that is termed "passivity towards precipitants". In the case of the iron and alumina mordants, the acetates give up the hydroxide more readily than the sulphates, the converse being, however, the case here. The chromium acetates are so difficult to decompose that they cannot be used like the acetates of alumina and iron.

A further peculiarity of the chromium salts is that they exist in two modifications, one violet and the other green, which differ in their behaviour towards precipitants and also in mordanting. The cause is due to their different constitution. According to A. Werner, the green chromium chloride contains two chlorine atoms in direct combination with the chromium, whereas in the violet chloride all three atoms of chlorine are precipitable by silver nitrate in the cold, and therefore cannot be regarded as directly combined with the chromium. The transference of the first modification into the other is an easy matter.

The aforesaid passivity towards precipitants was for a long time a hindrance to the employment of the chromium salts as mordants for cotton.

The chrome mordants consist of the following salts: Chromium acetate, bisulphite, fluoride, basic chloride, alkaline chrome solutions, potassium and sodium bichromate, and chromic chromate. Unlike the corresponding salts of iron and alumina, chromium sulphate and chrome alum are unsuitable for mordanting wool, the dyeing being irregular unless plenty of potassium bitartrate is used as well. Wool can, however, be very satisfactorily mordanted by means of 7 per cent. of chrome alum and 3½ per cent. of oxalic acid. Moreover, chrome alum—which is a by-product in the manufacture of alizarine, and is cheap—can frequently be used for chroming after dyeing. It is also an initial material for the production of other chrome mordants.

Chromium acetate is produced, by double decomposition, from chrome alum and lead acetate. As was the case with aluminium acetate, the product is not the normal acetate but a sulphacetate, and only about one-half to two-thirds of the sulphuric acid present in the chromium sulphate is precipitated. These compounds are almost exclusively used as chrome mordants for steam dyes in calico-printing; for mordanting cotton their use is restricted to piece goods.

The above-mentioned properties of the chromium salts are exhibited in a high degree by the various chromium acetates. The green solutions undergo gradual conversion into the violet form, the latter being more difficult to decompose. The behaviour of these salts, therefore, alters during storage; they have also the property of dissolving lead sulphate, this power increasing with their basicity.

Similar behaviour is exhibited by the chromium sulphocyanides, which, however, are rarely used (in calico-printing) as mordants.

Chromium bisulphite is prepared by treating a solution of chrome alum with an excess of sodium bisulphite or calcium bisulphite, and is used in mordanting cotton piece goods, for which purpose it is the most suitable of any of the chrome mordants.

Chromium fluoride, like the bisulphite, has only recently been introduced into practice as a mordant, and is now highly esteemed for treating wool, being especially valuable in cases where the oxidising action of potassium bichromate renders this latter unsuitable. An additional advantage of the fluoride is that it mordants the wool fibres in a very ready and uniform manner, without affecting their spinning properties or the feel of the resulting goods. It is used both for mordanting before dyeing and for after-chroming (see Mordant Dye-Stuffs), the mordanting bath in the former case consisting of 4 per cent. of chromium fluoride and 1 to 2 per cent. of oxalic acid (counted on the weight of the goods), and the operation being performed in the same manner as for wool in general.

Chromium fluoride corrodes both glass and metals, and must therefore be stored in wooden vessels. When employed in copper dye vats, its action on that metal may be prevented by hanging strips of sheet zinc in the vessel.

A basic chromium chloride may be prepared by dissolving chromium hydroxide in chromium chloride, and is used for mordanting silk and cotton yarns. In mordanting silk (according to the recipe of the Badische Anilin & Sodafabrik) the goods are immersed for six hours in a 20° B. solution of chromium chloride, then washed in plenty of water, treated in a cold bath of 1° B. sodium silicate for a quarter of an hour, unrolled, and carefully washed.

The mordanting of cotton yarn with this reagent is effected in two ways: in one, the yarn is impregnated with the mordant solution, dried, and passed through a boiling hot solution of soda; whilst in the other, the hydroxide is fixed by the aid of tannic acid or oleic acid. (See Fixing Agents.)

Alkaline chrome solutions are obtained by dissolving chromium hydroxide in caustic soda, or by treating a dissolved chromium salt with sufficient caustic soda to redissolve the precipitate first formed. On account of their strongly alkaline reaction, their use is restricted to cotton. This fibre is mordanted by impregnating it with a solution of this kind and leaving it to stand for twenty-four hours, finally washing with water to get rid of the excess of the solution.

Potassium bichromate, often called "chromate of potash," is the most important of all the chromium salts, and plays a great part in the dyeing and printing of fabrics, its applications being many and varied. As a mordant its employment is restricted to wool, for which it forms the principal reagent of this class.

The chroming of wool has been the subject of considerable study, the results obtained being as follows: If wool be mordanted by bichromate alone, the material absorbs chromic acid, leaving a normal chromate behind in the bath. Since the composition $K_2CrO_4 + CrO_3$ must be ascribed to the bichromate in aqueous solution, the wool apparently takes up only the free chromic acid present, and therefore it is usual to increase the activity of the bath by an addition of sulphuric acid, which liberates chromic acid from the normal chromate, this extra acid being then absorbed by the wool:

$$K_2CrO_4 + H_2SO_4 = CrO_3 + K_2SO_4 + H_2O.$$

Thus rather less than 1 part by weight of sulphuric acid is required (theoretically) for 3 parts of bichromate; and this proportion is employed in practice, inasmuch as the solution used contains 3 per cent. of bichromate and ½ to 1 per cent. of sulphuric acid (calculated on the weight of wool) with a 30 to 40-fold quantity of water. For very dark shades—especially when dyeing with polyoxyanthraquinone dyes (alizarine cyanines, etc.)- 4½ per cent. of bichromate and 1½ per cent. of sulphuric acid are used. The bath is never exhausted; a considerable quantity of chrome being left behind.

The precise form in which the chromic acid is contained in the wool is unknown, but, from the yellow colour of the mordanted fibre, it is assumed that a portion of the acid is in the free state. On prolonged storage, especially exposed to light, an appreciable reduction to chromic oxide occurs, and this circumstance may lead to subsequent irregularity in dyeing.

It is assumed that the mordanting action of the chromic acid is confined to the portion reduced to the state of chromic oxide by the wool and the dye-stuff.

The method described is but seldom advantageous, more handsome colours being obtained when the sulphuric acid is replaced by potassium bitartrate or oxalic acid. In such event, as may be concluded from the green colour of the mordanted wool, a much more extensive reduction of the chromic acid to chromium hydroxide occurs; and that this is actually the principal effect of these adjuncts is evident from the fact that these two reagents may be successfully replaced by other organic substances. Finally, mention may be made of the following fact: When wool mordanted with bichromate and sulphuric acid is treated with a reducing agent, such as bisulphite, it turns green, and then gives the same results in dyeing as though mordanted with bichromate and bitartrate. For this purpose the wool may be treated with 5 per cent. of commercial bisulphite solution for ten to fifteen minutes in a lukewarm bath.

The circumstance that wool mordanted with bichromate and sulphuric acid generally furnishes dull colours may be explained by the assumption that the chromic acid oxidises a portion of the dye-stuff to discoloured products. This method, however, is now practically abandoned, because of its weakening effect on the wool; and it is only used in exceptional cases; *e.g.* for alizarine yellow GGW.

The adjuncts, bitartrate and oxalic acid, do not behave alike, the former usually giving purer colours than the latter, and being therefore more often used, notwithstanding its higher price. A purer, semi-crystal form of the bitartrate is employed for specially brilliant shades. The mordant for dark tones consists of 4 per cent. of potassium bichromate and 3 per cent. of bitartrate, whilst for lighter shades 1 per cent of each is taken.

In some cases the other adjuncts to the chrome bath are equal, and even superior, to bitartrate, thus in mordanting hat bodies for light shades, oxalic acid is preferable on account of its cleansing properties; for dark shades with alizarine red and alizarine orange, sulphuric acid is the best adjunct to the bath, as giving colours very fast to milling.

Latterly, a whole series of new substitutes for tartaric acid have been introduced with more or less success. The best of these is lactic acid, which effects the complete absorption and reduction of chromic acid. The mordanting mixture consists of 2 per cent. of bichromate of potash and 3½ per cent. of lactic acid (or 4 per cent. of potassium lactate). Ammonium lactate is also used.

Vegetalin is a useful tartaric acid substitute, introduced by Lehmann & Voss (Hamburg) and G. Becker & Co. (Kempen).

The A. G. für Anilinfabrikation, Berlin, recommends the use of sulphate of ammonia in mordanting with bichromate of potash, the former salt being gradually decomposed, by the heat of the bath, into ammonia and sulphuric acid, thus ensuring uniform mordanting. The preparation for this purpose is known as metachrome mordant.

Formic acid, which of late years has come into use in dyeing, merits careful attention, since it ensures very complete utilisation of the bichromate bath, so that 1½ to 2 per cent. of bichromate of potash (and 2 per cent. of 80 per cent. formic acid) will be sufficient for even very deep dyeings. The distribution of the dye, also, is very uniform.

A consideration of some practical importance is the fact that light shades are rendered faster towards light, when mordanted with chromium fluoride than with bichromate and one of the above adjuncts. The only explanation of this is by the assumption that wool mordanted with bichromate always retains part of the chrome as chromic acid, which then acts destructively on the dye in presence of light.

Bichromate is an important agent in cotton-dyeing and calico-printing; it is used as an oxidising agent for aniline black, for catechu dyeing, to improve the fixing of certain tannin dyeings, as a discharge for vat blue, and finally for the production of chrome yellow and orange on the fibre.

Sodium bichromate is very similar to the potassium salt, from which it differs only in its hygroscopicity, ready solubility, and cheapness; it may therefore advantageously replace potassium bichromate. The commercial grade of this salt is of variable composition, and should therefore always be checked by analysis.

Chromic chromates are put on the market in three marks—GA I, GA II, GA III by the Höchst Farbwerke, the two first grades being suitable for mordanting cotton by the following method: Before use, the mark GA I is diluted with 2 to 4 parts of water, the goods being then immersed for twelve to twenty-four minutes, and carefully washed with water. Before rinsing, it is advisable to treat them with a weak (½ per cent.) solution of soda for twenty to thirty minutes at 60° C. Piece goods are impregnated with the solution by padding, then wound on a roller and left covered up, the remainder of the treatment being as already described.

The GA II mordant can be fixed on the fibre by a gentle steaming or hanging in the oxidising chamber, and is better adapted for piece goods. The mordant is diluted with four times its own volume of water, and receives an addition of 8 to 10 per cent. its volume of glycerine; in this solution the goods are padded, then steamed for ten to twenty minutes without pressure, and finally treated as in the preceding case. Both these mordants are sensitive to light, a circumstance that should be borne in mind when they are being used.

Finally, the mark GA III is recommended for wool-printing and for mordanting silk, the latter being steeped for twelve to twenty-four hours in the mordant solution (previously diluted with about four volumes of water) and washed after lifting.

Chromalin (Eberle & Co., Stuttgart) is a preparation which, according to the Patent specification, is obtained by treating acidified bichromate solutions with glycerine, carbohydrates, etc. Complex organic chromium compounds are probably produced, and these, when dissolved in a little acid, furnish an easily fixed chrome mordant, specially suitable for the Vigoureux method of printing, in which a short steaming is beneficial.

Tin Mordants. As independent mordants the tin compounds are of inferior importance; they are used for producing bright yellows with natural dye-stuffs, for cochineal scarlet on wool, to improve the brightness of alizarine red on cotton, and for a fast acid red with santal-wood on cotton (in mixed wool and cotton goods). The chief of these salts are the chlorides (stannous chloride or "tin salt," and stannic chloride) and sodium stannate.

Stannous chloride is the most important mordant for wool. The bath is prepared with 1½ to 4 per cent. of stannous chloride and 2 to 4 of oxalic acid or bitartrate, and the operation is generally conducted by the single-bath method. The use of tin mordants, however, lowers the capacity of the dyes for resisting the action of the milling process.

In the case of silk, stannous chloride is used, not for mordanting, but for loading the fibre in black dyeing with cutch (catechu); whilst for cotton it is employed to brighten the colour in turkey-red dyeing.

By reason of its reducing action, stannous chloride forms an important discharge in calico-printing. It is also used in the production of the so-called "carmines," *i.e.* colour lakes prepared by precipitating dye-wood extracts with stannous chloride.

A certain amount of care is required in dissolving this salt in water, owing to its tendency to separate out, in part, in the form of an insoluble basic salt ($SnOHCl$). The best way is to dissolve in a minimum of water and hydrochloric acid, in an atmosphere of carbon dioxide.

Stannic chloride (tetrachloride) is the chief tin mordant for cotton and silk. On cotton it is fixed by the aid of tannic acid (*q.v.*). The method of mordanting silk with this salt though seldom used is as follows: The silk is steeped for one hour in a clear 32° B. solution of stannic chloride, after which it is well washed with water and treated in a hot bath of soap and soda or of the latter alone, according to the quality of the silk, — followed by another washing. Stannic chloride is very largely used for loading white or light-coloured silks. The method formerly adopted was that just described for mordanting with tin, but this has now been generally superseded by the following, which enables a heavier loading to be obtained. The silk, after passing the tin bath and the subsequent washing, is immersed in two baths at 50° C.—one hour in each the first consisting of an 8° B. solution of sodium phosphate, the second of a 6° B. solution of sodium silicate. By this means the weight of the silk is increased by 18 to 20 per cent.

This is, however, not the normal manner of operating, it being necessary to employ the said baths repeatedly in order to obtain a higher degree of loading. The treatment in the tin bath and phosphate solution is repeated, but the silica bath is only used once at the end of the process. If, for example, it is desired to load a China silk weft to 50 to 60 per cent. above par—*i.e.* above the original weight prior to scouring—it is entered three times in a tin bath, followed in each case by a phosphate bath, and finally by the silicate bath.

When it is a question of loading silk to a fixed limit, it must be remembered that Japanese silk "draws" better (that is, takes up more from a given bath) than China or Italian silk.

This phosphate-silicate method of loading has been supplemented in an important degree by the conjoint use of sulphate of alumina. This salt is employed in cases where an additional tin bath would give too much weight: for example, when the increase in weight is not desired to be more than about 10 per cent. In order to load a Japanese silk warp up to 50 to 60 per cent., one cannot give four pink and four phosphate baths as in the case of China silk, because the weight would come out too high, whilst three baths of each would be insufficient. In such cases, therefore, the third phosphate bath is followed by treatment with sulphate of alumina, and this in turn by another phosphate bath, a treatment with water-glass completing the process. Sulphate of alumina also plumps out the silk threads.

In the event of a batch becoming overloaded, the weight may be reduced by treatment with hydrofluoric or oxalic acid, as already mentioned in connection with scouring silk. Any patchiness resulting from the water-glass bath can be removed by ammonia.

This method of loading silk, which is said to have been introduced by Neuhaus about forty years ago, plays an important part in silk dyeing, and much has been written in its favour of late years. Heavily loaded silk has the defect of very soon growing brittle—oftentimes during storage—and especially when the reddish patches about which so much controversy has arisen, make their appearance. On the other hand, loading makes the silk threads plumper, and thus enables silk fabrics to be woven with less material (*i.e.* cheaper).

The quantitative determination of the extent to which silk has been loaded can be determined by the hydrofluoric acid method and others.

Formerly the so-called "pink salt" ($SnCl_4 2NH_4Cl$) was largely used for the same purposes as stannic chloride. A crystallised chloride ($SnCl_4 5H_2O$) is also sold under the above title.

Sodium stannate is frequently styled "preparing salt," owing to its employment in preparing fabrics for printing. Its chief use is in printing woollens, its employment for cottons being now mainly confined to the so-called "Luccas".

Jute, also, is often prepared for printing by the aid of sodium stannate, the fabric being first padded with a weak solution of this salt (then dried, in the case of vegetable fibres), and then passed through dilute sulphuric acid, which precipitates stannic acid on the fibre. The process concludes with a thorough washing.

Sodium stannate is often used to brighten the colours in turkey-red dyeing.

Various tin mordants, formerly playing an important part in dyeing under the name of "tin solution" can be obtained by dissolving tin in different proportions of nitric and hydrochloric acid. At present only one of these is used to any extent (for producing cochineal scarlet on wool), *viz.* the so-called "scarlet acid". This is prepared in various ways, the following recipe, however, giving a mordant that produces an excellent scarlet: 16 parts by weight of tin are dissolved in 50 parts of nitric acid, 15 parts of hydrochloric acid, and 78 parts of water, the metal being added by degrees. As considerable heat is evolved by the reaction, the mixture will require to be cooled when prepared in the summer.

Of the other compounds of tin, the following find a limited application in calico-printing as adjuncts for steam alizarine red, in order to enliven the colour and protect it against the dulling effect of iron: Tin hydroxide, in the form of "tin paste" (prepared from stannic chloride and soda); tin sulphocyanide; tin acetate (prepared from stannous chloride and lead acetate, or by dissolving stannous hydroxide in acetic acid); and tin oxalate (by dissolving stannic hydroxide in oxalic acid).

Copper Mordants.—These mordants play a small but important part in dyeing, their colour lakes being extremely fast, if not particularly handsome. At present copper mordants are rarely used alone, but are mostly associated with iron or chrome mordants in black-dyeing wool and cotton, in dyeing cotton with cutch, and for a few single-bath, brown-dyeings with natural dye-stuffs on wool. In some of these cases, *e.g.* cutch, they act not merely as a mordant, but also as an oxidising agent.

It is worthy of particular note that the fastness of many mordant dyeings is improved by using copper in the mordant.

Copper sulphate, or blue vitriol, is the only copper salt employed for the above purposes. In dyeing with aniline black, and as a reserve under vat blue, it acts solely as an oxidising agent; finally, it also serves for "coppering" with many substantive dyes, in order to increase their fastness to light; its action in this connection has not been elucidated.

Of the other copper compounds, the sulphide is used as a carrier of oxygen in dyeing with aniline black.

Amongst other metals, mention may be made of zinc, nickel, lead, manganese, lime, and magnesia. Zinc gives good colour lakes with a number of dye-stuffs, but the only form in which it is used in practice is as zinc sulphite for alizarine steam blue in calico-printing, in which case it furnishes a handsomer though less stable colour than is obtainable with chrome mordants.

The salts of nickel have several times been proposed as mordants for alizarine, but their high price has hitherto hindered their use. They are sometimes employed for alizarine blue in calico-printing, the dyeings being handsomer than those with chrome mordants.

Lead was in use for some time in fixing eosine dyes on cotton, but does not give very good lakes, and at the present time only the acetate is of practical importance, this salt being employed in the preparation of other acetates, for chrome yellow and orange, and as an adjunct to reserves under vat blue. Of late a titanium lactate mordant—Cori-chrome—has been recommended for dyeing leather.

The supplementary mordants already referred to comprise salts of lime, magnesia, manganese, and zinc. In some dyeings—alizarine red, for instance—lime in particular plays an important part, its presence being essential to the mutual combination of the alizarine and the alumina. In other cases, *e.g.*

many steam dyes in calico-printing, the supplementary mordants serve to increase the fastness of the colours produced by the aid of other mordants. They are used in the form of acetates.

Manganese salts are used solely in the production of a brown colour, manganese bistre. Finally, in the form of potassium permanganate, this metal finds employment as a bleaching agent.

THE FIXING AGENTS (ACID MORDANTS).

I. The Tannic Acids. II. The Oleic Acids.

A whole series of bodies, such as tannic acids, many oleic acids, albumin, precipitated silica, etc., have the property of fixing a certain class of dye-stuffs on cotton, for which they otherwise have but a slight affinity. Of the foregoing substances only the first three are of any practical importance, and one of them, albumin, will be described later, its use being restricted to calico-printing.

The tannic acids and some oleic acids play a very important rôle in the dyeing and printing of cotton, where they are used for fixing basic dyes and mordants. Their mode of action is only partly understood, though the formation of an insoluble tannic or fatty acid compound of the metal must be assumed when a metallic oxide is fixed by the aid of a tannic acid or a fatty acid. However, in the case of fixing basic dyes, no chemical combination between the colour base and the tannic or oleic acid is probable. At all events, the part they play is not so important as that of the mordants in the case of the adjective dyes, and for this reason they have received the distinctive title of "fixing agents," though some colour chemists, in the assumption that a combination occurs between the colour base and the tannic or oleic acid, class them as "acid mordants".

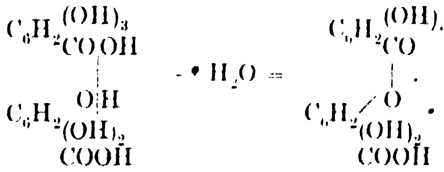
1. The Tannic Acids.

The vegetable kingdom furnishes a number of substances possessing very similar properties. They have an acid character, and act as precipitants of egg albumin, gelatine, alkaloids, etc. A few of them are used for tanning leather, on which account they have received the group name of "tannins" or "tannic acids".

The chief tanning materials are oak bark, gall nuts, cutch, sumach, chestnuts, myrabolans, divi-divi, etc.

Gall nuts are diseased excrescences produced on various plants, notably the oak tree, by insect punctures. They furnish the best-known and, for the dyer's purpose, the most important of the tannic acids, *viz.* tannin, which is obtained by extraction with water, alcohol, and ether. The tannin is chiefly in the aqueous extract, and is recovered by evaporation. On evaporating to dryness a solution of tannin, to which alcohol and ether have been added, the slowly thickening liquid froths up under the influence of the escaping vapour and finally leaves a very loose mass, which comes into commerce as powdered tannin, and is held in high esteem on account of its ready solubility in water. "Tannin in needles" is the commercial crystalline form, and is prepared by evaporating to syrupy consistence a solution of tannin, drawing it out into threads, drying these on heated metal drums, and finally comminuting the product.

Gallotannic acid contains as its most active ingredient a digallic acid, resulting from the condensation of two molecules of gallic acid. This condensation was formerly assumed to proceed on the following lines:—



but since the discovery that tannin is an optically active substance and must therefore contain an asymmetrical carbon atom this formula can no longer be regarded as accurate.

Cutch, or catechu, is employed as a dye-stuff and tanning material.

Sumach is composed of the leaves and twigs of a shrub of the Rhus family, the best quality being furnished by *Rhus coriaria* (Sicily, Spain, the Balkans, etc.). Latterly it has also been sold in the form of a 30° B. extract. It contains gallotannic acid.

Chestnut extract is obtained from the wood of the horse-chestnut.

Myrabolans are the fruit of various trees (*Myrabolanus chebula*, etc.) occurring in China and the East Indies.

Divi-divi is the name given to the fruit of *Cæsalpinia coriaria*, Willd., found in the West Indies and South America.

Of all these substances the most important for the dyer are tannin, sumach, and cutch; of the rest, chestnut extract is principally used in black-dyeing silk.

All tanning materials exhibit a tendency to turn, on oxidation, into yellow or brown dye-stuffs, which have an affinity for cellulose. They are all therefore more or less strongly coloured, except tannin, which can be prepared quite colourless, and is therefore the only one that is suitable to use for light and bright shades. Of late, however, a decolorised sumach extract has been put on the market, and is adapted to replace tannin in most cases.

When exposed to the air, dilute solutions of tanning materials oxidise and deposit a brown precipitate, and therefore should not be kept stored.

In working with tannic acids, care should be taken to keep them out of contact with iron, since they form a dark-coloured compound with that metal.

Application of Tannic Acids to Cotton.

The employment of these substances in cotton-dyeing is principally based on their absorption by this fibre. On cotton being immersed in an aqueous solution of tannin, a portion of the tannic acid is gradually and uniformly taken up by the fibre. After some time the absorption ceases, a state of equilibrium then existing in respect of the distribution of the tannic acid between the water and the fibre. In any case, the amount absorbed is only very small, the absorption being least at boiling-heat, and most at a not very precisely determined medium temperature of about 40° C.

Other factors influencing the absorption are—the quantity of water, tannic acid, and cotton present, the influence being exerted in a very regular manner, which is quite analogous to the absorption of dye-stuffs by textile fibres, and in accordance with the law of distribution which will be more fully discussed in dealing with the theory of dyeing. The higher the proportion of tannic acid and the lower that of water taken, in comparison with the amount of cotton present, the larger the quantity of tannic acid absorbed. The necessary consequence of this behaviour is, that the fixing baths must contain as little water as is compatible with the dissolving of the tannin or sumach.

If the cotton be washed with a large volume of water after passing through the tannin bath, nearly all the absorbed tannic acid will be driven out again, and consequently no more than a gentle rinsing is permissible.

Cotton treated with tannin is then capable of fixing basic dye-stuffs, inasmuch as it takes up the colour base and leaves the acid behind in the bath. Both these dyeings and the precipitates ensuing on treating the corresponding dye-stuff solutions with tannin, are soluble in water as well as in an excess of tannic acid; consequently, the tannic acid salts of the colour bases cannot be fixed on the fibre. However, if the cotton be treated in a solution of a metallic salt after passing the tannin bath, there is formed an insoluble metallic tannate, firmly adherent to the fibre, and far more capable than free tannic acid of absorbing basic dyes from solution, and fixing them so as to stand washing. Whether under these conditions there occurs any chemical combination with the tannic acid attached to the metallic oxide is unknown, and is, moreover, improbable, since the absorption of the colour bases goes on with great readiness, even at the ordinary temperature.

This important method of fixing basic dyes on cotton was discovered by John Dale and Thomas Brooke in the "sixties". It is generally effected by the aid of tartar emetic as the metallic salt, the operation being performed in the following manner: The cotton or cotton yarn is first well damped with hot water, and then left overnight in a hot solution of tannin or sumach, the amount of tannin varying according to the depth of colour in view and the nature of the dye-stuff to be used—

within somewhat wide limits: about 1 to 10 per cent. of the weight of the yarn, the usual amount being 2 to 4 per cent. For darker shades sumach is used; and it may be taken for granted that 3 to 4 parts, by weight, of sumach extract are equal to 1 part of tannin. Sufficient water should be used to just cover the yarn, and a hot bath has the advantage of expelling all the air out of the material, and thus facilitating impregnation. Moreover, in this case the gradual cooling of the bath during its sojourn overnight will enable it to retain for a longer period the medium temperature already mentioned as the most favourable for the absorption of tannic acid by cotton.

After the cotton is taken out of the bath, it is well drained, and is then worked about in a bath containing, on the average, 1 to 2 per cent. of tartar emetic, *i.e.* about half the weight of the tannin used, and is finally washed with care. According to results obtained by Falke, only ½ per cent. of tartar emetic is required to fix 2 per cent. of tannin, and only 1 per cent. to fix 6 per cent. of tannin, thus showing that a large excess of tartar emetic is used in practice. This is, however, no particular drawback, as it ensures the thorough fixation of the tannin; and as the tartar emetic bath is used over and over again, there is no waste of antimony.

After a slight tannin treatment, the cotton is only left in the tartar emetic bath for about ten minutes, the time being increased from a quarter to half an hour when a stronger tannin bath has been used. The rapidity of the fixing process is in direct ratio to the concentration of the tartar emetic solution.

Cotton piece goods should not be left to stand in the tannin solution, but are wound through a 5 to 20 per mil. solution of tannin by means of a jigger (*q.v.*) for some time, and then treated in the same way in a strong solution of tartar emetic; or the pieces are drawn through a warm concentrated solution of tannin, then wound up on a roller, left to stand for one to two hours, and fixed in the same manner as before.

Although the process of fixing with tannin and tartar emetic has been known and practised in various ways for a long time, some uncertainty still prevails as to the best temperature for the tannin bath, and the time required for arriving at the state of equilibrium in the distribution of the tannic acid between the fibre and the water. The tartar bath is used cold, lukewarm, and hot, and equal uncertainty prevails as to the best temperature for the formation of the antimony tannate, and the amount of tannin to be brought on the fibre, in any given instance. Weber, it is true, elaborated a method for estimating the amount of tannin required to ensure the complete precipitation of the different basic dyes from solution ; but the method itself is difficult of performance, and, besides, necessitates the previous determination, in each case, of the amount of tannic acid taken up by the cotton.

Since the badly fixed dyeings with basic dyes on cotton are of very low stability, it is always well to use more tannin and antimony than are absolutely needed, the baths being used again. In the case of the tannin bath, the liquor may be recuperated by adding a very small fraction of the original charge, the quantity adsorbed being so small. The tartar emetic bath should always contain a readily detectable amount of antimony, and be free from acidity and dirt. The water used for dissolving the tartar emetic should be pure. Acidity in this bath is the result of an accumulation of potassium acid tartrate, owing to the absorption of the antimony by the cotton. It may be neutralised by an addition of chalk, which is preferable, for this and similar purposes, to any other alkaline substance, inasmuch as it dissolves only just in the same proportion as the acid salt is formed. Old tartar emetic baths contaminated with dissolved dye-stuffs must be clarified by settling or filtration before being used again.

The tannin and antimony fixing process has not suffered much alteration since its first introduction. Other organic acids, *e.g.* benzoic acid and phthalic acid, are able to fix basic dyes on cotton ; but the colours obtained are deficient in fastness, though handsome, so that none of these substances has found any practical application. For some time zinc sulphate was used to replace tartar emetic in fixing tannin ; but the colours were less fast, and, indeed, no other metal is as good as antimony for this purpose. Other antimony compounds equally as suitable as tartar emetic are antimony hydroxide, potassium-antimony oxalate, and antimony fluoride, in the form of double salts, etc., which have been frequently recommended as "tartar emetic substitutes," and employed as such.

Antimonyl potassium oxalate ($SbK_3(C_2H_4)_3 . 4H_2O$) may be used to replace tartar emetic, weight for weight, notwithstanding its far smaller percentage of antimony; and, being readily soluble, is also suitable for reserves under basic dyes.

The introducers of the last-named salt (Koepp & Co., of Oestrich-on-Rhine) have also put on the market a double fluoride of antimony and sodium ($SbF_3 . NaF$) as a substitute for tartar emetic; 658 parts by weight of the new salt being equivalent to 1000 parts of the old.

The "antimony salt" of E. de Haen (List, near Hanover) corresponds to the formula $SbF_3 . (NH_4)_2SO_4$, and 9 parts are equivalent to 10 parts of tartar emetic.

The double fluorides of antimony are strongly acid, and must therefore be neutralised before use.

Boehringer's "Antimonin" is a mixture of antimony and calcium lactates.

A peculiar method of fixing basic dye-stuffs with tannin, which, however, is hardly likely to find general application, is that devised by the Höchst Farbwerke, for Janus dyes. The material is dyed with Janus blue, with gradual addition of zinc sulphate and common salt, and is then treated, in a second bath, with tannin and finally with tartar emetic. In dyeing light shades, for which the method is best adapted, the tannin may be used in the dyeing bath, a little hydrochloric or acetic acid being present; and the goods are fixed with tartar emetic, either in the same bath or a separate one.

The property of tannic acid for forming, with the metallic mordants, insoluble salts that adhere to the fibre of cotton renders it very valuable as a fixing agent for mordants, the method of application being to first treat the cotton in a bath of tannin or sumach and then in a cold solution of the mordant used. Iron, tin, and alumina are fixed on the fibre in this manner, the method being chiefly valuable for yarn-dyeing.

For fixing iron, the following procedure is adopted: The cotton, after being treated with sumach, is passed through lime water and then immersed in the iron mordant solution for a quarter of an hour to an hour, according to the amount of sumach used, the process concluding with a washing, preferably in hard water or water containing chalk, to neutralise the acid. The lime bath treatment produces calcium tannate, the neutralisation of the acid thus facilitating the formation of iron tannate in the subsequent iron mordant bath. The method is modified in various ways, the lime-water treatment sometimes following the iron bath, whilst in other cases chalk is added to the iron bath itself. The iron mordants used for this purpose are ferrous sulphate, pyrolignite, and nitrate, a few degrees Baumé in strength. As iron tannate is of a greyish colour, the cotton treated in this way will also be grey or black, which is the reason why the use of iron in this connection is restricted to the production of dark shades. Blues fixed with tannic acid and antimony are often passed through an iron solution when required to be darkened. Iron tannate is also employed as an independent dye, an iron-grey of this kind being produced in yarns, notwithstanding that it hardens the fibre. The only use for iron, fixed with tannic acid, as a mordant is in black-dyeing.

For mordanting with tin, the cotton, after passing through the tannin bath, is treated for about half an hour in a cold solution of stannic chloride (2 to 5° B. strength) and then washed with water containing lime.

As a fixing agent for alumina the sole use made of tannic acid is in Turkey-red dyeing (*q.v.*), where it is employed to make the colour lake faster.

Application of Tannic Acid to Silk.

In silk-dyeing, tannic acid is used for loading the fibre, fixing the iron, and solidifying the colour.

Except in the case of light shades, the loading of silk by tannic acid is effected solely by the aid of sumach extract or chestnut extract. Some prefer to load after dyeing, but generally the loading and dyeing are combined in the same bath. The most favourable temperature for the absorption of tannic acid by silk is about 70° C.

For ordinary black-dyeing on silk (*q.v.*) the tannic acid is supplied by catechu, which serves both as a loading material and as a fixing agent for the iron. Souple silk is often loaded, and simultaneously mordanted with iron, by alternate treatment with a solution of tannin (principally chestnut extract) and a bath of iron pyrolignite. After the iron bath the silk is exposed to the air for a short time (about half an hour) in order to oxidise the ferrous tannate. The treatment with tannin and iron is often several times repeated, the strength of the later tannin baths being increased, and the operation being concluded with a washing in hard water. After repeated use the iron baths become acid through the liberation of pyroligneous acid, which is then neutralised by an addition of iron filings enclosed in a bag.

The solidifying process is employed to improve the fastness of the dye, and is performed by immersing the dyed silk in a lukewarm 8 per cent. tannin bath until the latter has become cold, whereupon the silk is washed, passed through a 4 per cent. bath of tartar emetic, again washed, and finally revivified. (See Dyeing.)

In the case of wool the tannic acids are very little used, and then only in the form of sumach for a few single-bath dyeings with natural dyes. (See Mordant Dyes.)

2. The Oleic Acids.

These substances are almost exclusively used for cotton. The earliest application of fatty bodies in dyeing occurred in the Turkey-red industry, which, even at the present time, consumes large quantities, chiefly of the sulphonated "tournant" oil class, to perfect the fastness of the colour by fixing the alumina of the colour lake, etc. (See Turkey-red.)

The so-called Turkey-red oil was first introduced about the middle of the nineteenth century. It is prepared by treating olive oil or castor oil (ricinus oil) with concentrated sulphuric acid. A preparation of this kind was recommended for Turkey-red dyeing by Runge in 1834; but it did not find employment until the sixties, when it came into use for printing with basic dye-stuffs, the goods being prepared with sulpholeate for printing, or else use was made of the printing pastes, containing Turkey-red oil, supplied by some makers. Afterwards it was employed as a preparation for steamed alizarine dye-stuffs (N. Ziegler), and by H. Koechlin (in 1874) for alizarine dyeing. Still later, sodium sulphoricinate -imported at that time from England--and ammonium sulphoricinate first prepared by F. Storck- came on the market. The proportions employed in practice vary from 1½ to 4 parts of acid per 10 parts of oil, more acid being used in winter than in summer. The method of procedure is, however, the same all the year round, the acid being poured slowly into the oil, with constant stirring and then left to stand until a sample of the product is found to dissolve completely in water, whereupon the whole is poured into water and washed with a solution of common salt to remove the excess of sulphuric acid. The residual acid is neutralised with soda or ammonia.

While the acid and oil are being mixed, the temperature must be prevented from rising above 40° C., since otherwise the acid will exert an oxidising action, a condition revealed by the copious evolution of sulphur dioxide, in which case the product will be dark in colour and furnish poor results in dyeing.

Good Turkey-red oil should dissolve to an almost perfectly clear solution in water; any slight turbidity formed can be removed by the aid of ammonia.

As the name indicates, Turkey-red oil is mainly used in Turkey-red dyeing, where it serves to increase the brightness and fastness of the colour. Its composition formed the subject of numerous investigations by Liechti and Suida, Muller-Jacobs, P. Juillard, and many others, who devoted a great deal of attention to a thankless task in the hope of elucidating the process of Turkey-red dyeing. It is found that by the action of sulphuric acid on castor oil, under the conditions prevailing in the production of Turkey-red oil, a large proportion of the oil is left unaltered, whilst another portion furnishes a sulphoricinoleic ester and ricinoleic acid; in addition, sulphonated glycerine ether and polymerised compounds (polyricinoleic acids) may also be formed, according to the conditions (temperature[1]) of the operation. According to Herbig, the effectiveness of Turkey-red oil is improved when only a certain percentage of the oil is saponified in the manufacturing process. He also considers that glycerine probably in the free state is present only as such, and that, when olein from oleic acid is used, stearosulphonic acid is formed, which, when the oiled goods are dried, oxidises into oxystearic acid, which he regards as the really active constituent of Turkey-red oil.

That the various constituents of Turkey-red oil, however, have little practical effect in Turkey-red dyeing was first demonstrated by P. Lochtin, who obtained with an acid ammonium ricinoleate just as good a red as with Turkey-red oil. Similar "acid soaps," obtained by treating a dissolved soap with a quantity of acid just insufficient to produce separation of the fatty acids, are now largely used to replace Turkey-red oil. According to Schlieper, they are even preferable to Turkey-red oil, because they are not so liable to decompose on standing. It would seem that the practical value of the use of sulphuric acid in preparing Turkey-red oil from castor oil is confined to rendering the latter soluble.

Turkey-red oil forms a good fixing agent for mordants, but its practical application in this direction is confined to the fixing of alumina by various methods. For Turkey-red, for example, the fibre is first impregnated with a strong solution of Turkey-red oil (by the same appliances as were used in the old red-dyeing process), and then dried, the cotton being afterwards immersed for some time in a solution of basic alum or aluminium acetate, and finally washed with water containing chalk (to neutralise the acid), followed by pure water. Piece goods are left rolled up for some time after passing the alum bath, to facilitate the fixing of the aluminium fatty acid salt.

The fixing process is also effected in other ways, a solution of soap being frequently used in place of the Turkey-red oil; for instance, the cotton is steeped for several hours in a solution of basic alum, then lifted, drained, and treated with a hot soap solution, followed by washing, the whole procedure being repeated if necessary.

Turkey-red oil can also be used for fixing basic dyes on cotton, but the resulting colours are less stable though more handsome, than those obtained by the tannin-antimony process. The goods may be impregnated with Turkey-red oil, and then dyed after drying; or, better still, the oil is fixed as above, with alumina. Practically, however, this method is only of value in the case of rhodamine, which dye-stuff gives only a dull lilac when fixed with tannin and antimony, but a beautiful rose-red when fixed with Turkey-red oil. In this special case the following method is adopted: The cotton is first treated for ten minutes in a 10 per cent. solution of Turkey-red oil, and, after draining and drying at a moderate heat, is worked about several times in a 6° B. solution of aluminium acetate (or aluminium sulphocyanide), followed by draining and drying. After rinsing, the mordanting operations are repeated in the same baths, and the goods slightly rinsed again, the dyeing being finished before they are allowed to dry.

Another very frequent use of Turkey-red oil is in the preparation of cotton piece goods for calico-printing (*q.v.*). That it also forms a good detergent was shown in the preceding chapter.

Monopol Soap.—Whereas even the most highly concentrated Turkey-red oils are fluid, Stockhausen succeeded in producing a solid preparation, a "gelatine soap" (containing about 95 per cent. of fat), by—it is stated—warming Turkey-red oil with a little more caustic soda than is required for neutralisation. This preparation, which is now largely used, under the name "Monopol soap," possesses properties which seem to make it superior to ordinary Turkey-red oil for many purposes. Thus, it is a better detergent, since it can be mixed with hard water without precipitating any lime or magnesia soaps—in fact it has a solvent action on these latter. When used to replace Turkey-red oil in dyeing it has no yellowing effect, and it is also better than Turkey-red oil in dressing fabrics, since it does not impart any smell of fat to the goods. It is also useful as a supplying agent.

Application of Oleic Acids to Silk.

These substances are used for two purposes in silk-dyeing, *viz.* for brightening the colours and for softening the fibre.

In the first case use is made of an emulsion of olive oil or "tournant oil," more or less strongly acidified. (See Acid Dye-Stuffs.)

For softening purposes, especially in the case of "souple" silk, the so-called "*deux huiles*" (two oils) are used, consisting of a mixture of equal parts of sulphuric acid and olive oil. The acid is poured slowly into the oil, which is kept rapidly stirred, the mixture being diluted with warm water when bubbles begin to form; and the silk is drawn through this bath for a short time, whereby it is immediately softened. The usual proportions are 2 per cent. of oil (calculated on the weight of the silk) and an equal quantity of acid. (See also Application of Acid Dye-Stuffs to Silk.)

CHAPTER IV.

DYEING.

FOR the sake of convenience, the diversified subject-matter of this chapter has been divided as follows:

I. Theory of colour; combination of colours; dyeing to pattern.

II. Theory of dyeing.

III. Classification of the dye-stuffs; methods of dyeing.

IV. Dyeing textile fibres on the large scale.

V. Trial dyeings; colorimetric determinations; reactions of dye-stuffs on the fibre; tests for fastness.

1. Theory of Colour; Combination of Colours; Dyeing to Pattern.

It is usual to regard the *colour* of any substance as a special property of that substance, inherent to and dependent on its nature solely. The chemist and physicist, however, know that one and the same substance may change its colour in accordance with its state of subdivision, metallic silver being black or golden yellow as well as white.

What we are accustomed to call the true colour of any object depends not upon itself alone, but on the eye of the observer and on the light rays by which the object is illuminated. Colours have no real existence, but are mere subjective impressions that we receive from the light falling upon the object in question. It is more than probable that no two persons receive exactly the same impression from the observation of any colour, even though they employ the same word to express it.

This divergence in the vision of colours may extend to colour-blindness, or the incapacity for distinguishing between widely different colours—generally red and green. A still more important part in this connection is played by light, since the colour of any object is nothing more or less than that portion of the impinging light that is reflected by the object. The light we have solely to consider is that of the sun, which is composed of light rays of all colours. If this light be allowed to fall on a glass prism it will be analysed into its constituents, the various light rays undergoing different degrees of refraction; and in this manner we obtain a coloured strip containing all the colours present in sunlight, each one separated from the others. These are known as "the colours of the spectrum," and if the same light rays be reunited we again obtain white light.

Again, certain colours of the spectrum will furnish white light if united in pairs; and such colours are termed "complementary colours," their arrangement being as follows:—

Red and bluish-green.
Orange and greenish-blue.
Yellow and blue.
Greenish-yellow and violet.
Green and red-violet.

White is therefore not a colour capable of physical definition, but is merely a mixture of sensations, a physiological phenomenon, caused by the incapacity of the human eye for analysing a mixture of various light rays as the ear distinguishes the several notes in a musical chord. This incapacity for distinguishing between simple and compound colours is not confined to white, but extends to all other colours as well, the eye receiving merely a total impression; in fact, so little is the organ in question capable of differentiating between colours simultaneously impressed on the retina, that the effect of a uniform colour can be produced by a skilful blending of several different colours, as is actually done in Parisian Gobelins fabrics.

Consequently, when we speak of the true colour of an object, this term merely implies that the object has the property of absorbing all the rays in sunlight except those corresponding to the said true colour. For this reason it will appear of a different colour if illuminated by another kind of light. Thus, for example, a red object illuminated by a white light compounded of blue and yellow rays will absorb both these colours, and appear to be no longer red, but black.

The colours of all terrestrial objects, as also of all natural and artificial dye-stuffs, are neither so homogeneous nor so intense as the colours of the spectrum. For instance, there is no single red that—like the red of the solar spectrum—consists solely of this colour without any admixture of yellow or blue. Again, since such colours lack the intensity of those of the spectrum, their mixtures do not furnish a white—like the complementary colours of the spectrum—but a more or less dark grey.

Grey is therefore a white of low intensity; whilst, considered from a physical standpoint, black is not a colour at all, its intensity being *nil*. Therefore, when we view a white surface the sensation of light is so intense that the formation of a clear conception thereof becomes difficult, such an effect being unattainable by our natural and artificial dye-stuffs. A further consequence of this is that the dye-stuffs or any other coloured materials destroy more of the impinging light than pure white bodies. Hand in hand with this absorption of light proceeds the absorption of heat by the colour, a circumstance that may account for the known faculty, possessed by the blind of distinguishing between colours by touch.

The comparative intensity of colours can be determined and expressed in numerical values by the aid of a very simple piece of apparatus. For this purpose a circular white disc is divided into four sectors, two of them being then painted a deep black, as shown in Fig. 24. On setting this disc in rapid rotation, the mixed impressions of black and white produce the sensation of grey, the intensity of which is evidently determined by the angle of the two white sectors. If we set down the intensity of white as 1 and that of black as zero, the grey resulting from the rotation of the disc in Fig. 24 will have the intensity $\frac{60}{360} = \frac{1}{6}$.

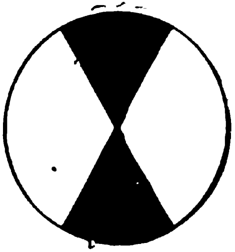


FIG. 24.

To measure the intensity of any colour, the two opposite sectors of a white disc are painted over with that colour, and the remainder of the disc painted with a complementary colour, the angles of the painted sectors being then varied until a grey is obtained on rotating the disc. By determining the intensity of this grey in the manner described above, we have a measure of the intensity of the two colours on the painted disc, when it is recalled that these intensities are inversely proportional to the dimensions of the angles of the respective sectors. Hence if the two complementary colours are of equal intensity, exactly one-half of the disc must be painted over with each in order to produce a grey on the disc being set in rotation. On comparing the various available colours by this means, their intensity will be found to vary considerably, there being, for example, no single blue, green, or violet equal in intensity to the yellow of lead chromate.

In everyday life, as also in the dyeing and printing industries, an entirely erroneous conception exists as to the meaning of the "intensity" of a colour, this being generally confounded with depth of colour—a totally different property. Thus, for example, if a blue be mixed with black, it becomes deeper in colour, but not more intense, the intensity of black being *nil*. In this way dark dyeings may be produced with a very little dye-stuff; and as the beauty of the colour is improved by the admixture of an *absolute* black, a black of this kind would be very valuable, provided it also possessed the other qualities demanded of a good practical dye-stuff. With such a black it would be possible to produce a series of dark shades much handsomer and more cheaply than is obtainable by existing methods. On mixing colours with blacks of the kinds now available, the following modifications are produced:—

Yellow with black gives brown.
Green ,, ,, olive.
Red ,, ,, red-brown.
Blue ,, ,, grey-blue.

If the intensity of the colours be reduced by applying them in thinner layers, they suffer a peculiar change of tone, becoming poorer in red. Thus orange becomes yellow, blue turns more greenish-blue, etc. Therefore, if it be desired to lighten a colour without altering its tone, it must receive an admixture of red.

The knowledge of which colours are complementary to each other is of considerable practical value. In dyeing textile fibres the colours are mostly produced by combining two, three, or even more dye-stuffs,—mode colours, for instance, being generally obtained by combining yellow, red, and blue, the dye-stuffs used having to fulfil two principal requirements: suitability for combination and good equalising properties. Most of the dye-stuffs of any one group will combine well together; but dyes that require a strongly acid bath will combine badly with such as have to be dyed in a neutral or weak acid bath. Equalising implies the uniform distribution of the dye throughout the fabric, etc., without difficulty.

In addition, however, certain other factors have to be considered, such as fastness to light, and the shade, brilliancy, and price of the dye-stuff; so that it is sometimes a matter of difficulty to fix upon the most suitable dyes for a given colour.

Occasionally in combination dyeing a hitherto unexplained phenomenon is noticed, some unstable dye-stuffs giving fast colours when combined with other dyes, *e.g.* the case with methyl-violet along with alizarine on cotton.

If a fabric be dyed with a blue, a yellow, and a red dye-stuff in certain proportions—entirely dependent on the properties of the dye-stuffs themselves, such as tone, productivity, and affinity towards the fibre—a grey will be produced. Hence these three colours should be complementary. However, yellow and blue have already been given as complementary, and should therefore suffice to give a grey when combined; the addition of red should consequently furnish a brownish-red. To find an explanation of this apparent paradox it should be remembered that the colours at our disposal are not homogeneous, green being present both in blue and yellow. On the two being mixed together, one complements the other and grey is formed, but now the green present in both makes itself apparent, and we have, instead of grey, a greenish colour.[1] Now, in presence of the red, this latter combines to form a grey, the red and green being complementary colours. If in such a combination the yellow preponderates, a yellowish-grey, drab, or brown will be produced, a predominance of blue giving a greyish-blue, and so on. The colours resulting from combinations of only two of these colours can be easily deduced; blue and yellow furnish green; blue and red, a bluish-red or violet; yellow and red, orange.

Knowledge of such combinations mostly finds its application in dyeing to pattern, which consists in producing a colour that shall exactly match a given pattern.

In many dyeings only a single dye-stuff is employed, but if the dyeing is to be strictly to pattern, the aid of other dye-stuffs has often to be sought in order to obtain the desired tint. Thus if in dyeing a blue, for example, the colour has come out rather greener than the pattern to be matched, it must be 'shaded off' by adding a small quantity of red or violet. A bluish-black can be shaded or converted into coal black by the aid of a yellow dye.

Occasionally, too, it is necessary to top a colour with a small quantity of another dye-stuff, particularly when it is desired to increase the brightness of the colour. In such event a bright dye of the same shade and with good equalising properties is used.

One circumstance in particular occasionally renders dyeing to pattern a really difficult task, namely, that a simple comparison with the pattern immediately after dyeing is not sufficient, it being necessary to take into consideration the changes the colour is likely to suffer in the subsequent operations of washing, drying, finishing, etc. This necessitates an accurate acquaintance with the behaviour of the particular dye-stuff in question —a knowledge only to be acquired by practice. Thus if it be known, for instance, that a given yellow dye has the property of becoming greener in the subsequent operations, then, in order to arrive at an exact match to the pattern, it will be necessary to dye at first somewhat redder than the required shade.

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[1] On mixing yellow and blue—not substantially, but in the state of the sensations produced by both colours on the retina—a grey is obtained, as may be demonstrated by the rotating disc aforesaid.

The comparison of a dyeing with the original pattern is known as "matching"; and in this operation the following considerations must be borne in mind :—

1. Colours have a different (generally darker) appearance on the wet material than on the dry fibre; consequently, in matching, a small piece of the dyed material must be taken and dried; though, with practice, wet matching is possible.

2. The general and particular appearance of the two specimens must be compared, so as to enable an *immediate* judgment to be formed as to their similarity or difference. The longer the eye looks at colours the less sensitive does it become to slight differences between them.

The samples should never be viewed by artificial light, but always by diffused daylight. Even in this case, however, one and the same colour will sometimes have a different appearance, this being more particularly observable in the case of certain aniline drabs on wool, which appear greener at one time and more reddish at another, according to the lighting of the place where the inspection is made.

The problem of matching colours by artificial light has been solved in a very satisfactory manner by the "Dalite" lamp of Dutton & Gardner. This is an electric arc lamp, the globe of which is coloured by means of copper.

Finally, it should be mentioned that in harmonising colours (in cloth-printing) the best results will be obtained when the colours in juxtaposition are mutually complementary; also, that the brighter colours ought to be allotted a correspondingly smaller space than the others, in order to prevent the total effect being spoiled by the predominance of one or two of the colours.

2. Theory of Dyeing.[1]

The two principal factors influencing the method of performing any operation of dyeing, and the behaviour of the colour when finished, are the dye-stuff and the fibre. Dye-stuffs behave variously in dyeing, the difference being dependent on their chemical composition and on the nature of the fibre to which they are applied.

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[1] The following sources have been drawn upon in compiling this section: Georgievics: *Mitth. Techn. Gew. Mus. Wien*, 1894, p. 165; *ibid.*, pp. 205-220, 349-361; *Monats. f. Chem.*, v. 15, pp. 705-717; 16, pp. 345-350; Lehne's *Färber Ztg.*, 1895-96, pp. 17-18; *Chemiker Ztg.*, 1895, p. 426.

The structure of the fibre, which influences capillarity, has also a notable, though not decisive effect on the course of the dyeing process.

An examination of the classified dye-stuffs shows that the mutual relation of the members of each class depends more on a single property held by them in common than on their constitution. Thus all the numerous acid dyes, be their constitution never so divergent, behave in a perfectly analogous manner when applied to the different textile fibres, and exhibit no fundamental differences. This they evidently owe to their acid character, due to the presence of sulpho-, nitro-, and hydroxyl groups, the last-named playing the principal part in this connection.

The basic dye-stuffs, whether azo compounds like chrysoidine or belonging to the triphenylmethane derivatives like fuchsine, all exhibit the same pigmentary character, thanks to the one or more amido groups present in each.

In case of the substantive dyes, the connection between their constitution and their behaviour in dyeing is still entirely uninvestigated.

In the case of the mordant, or adjective, dyes, the relation between their constitution and their capacity for dyeing mordants has not yet been thoroughly investigated. This much is certain, that here also the hydroxyl groups play the principal part, this property being due to a special quality, and not to their acid character alone, since otherwise the far more strongly acid sulpho groups would exhibit a similar influence, which is not the case, the capacity of a dye for fixing with mordants being diminished by the presence of sulpho groups.

In the reduced state, the vat dye-stuffs have for textile fibres an affinity which may be compared with that of tannic acid for cotton. During the subsequent oxidation, the original dye-stuff is re-formed.

The sulphur dyes most nearly resemble the vat dye-stuffs in their behaviour during dyeing, since, in their case also, reduction products, and not the dye-stuffs themselves, are taken up by the fibre.

The insoluble dyes, like the developing and albumin dyes, can only be compared with the other groups when in their developed and finished state.

At a very early stage the problem arose as to the fundamental cause of the production of the dyeing effect. One school regarded the process as purely mechanical, whilst the other looked upon it as a chemical process, consisting in a chemical combination between the dye-stuff and fibre.

Since then an immense amount of labour has been devoted to this question, without until recently much progress being made; a circumstance explainable by the peculiarity of this difficult task. A whole series of mechanical and chemical theories of the dyeing process have been established, in which the operation of dyeing is regarded either as being the same in all cases, or else as differing in principle for each class of dyeing.

The problem seems now to have attained a certain degree of solution, inasmuch as it is possible to regard all dyeings from a uniform standpoint, and, in part at least, to understand and explain them.

Before going more closely into the phenomena of dyeing, it is necessary to presuppose—as may be justifiably done, although direct proof is lacking that all dyeings which are performed under approximately similar conditions are based essentially on the same cause and therefore may be regarded as phenomena of the same order. If an experiment has been made, for example, in dyeing sheep's wool with a basic dye, and certain results have been obtained, it may be assumed that other basic dye-stuffs will behave in a similar manner with regard to the same material. In the case of the acid dye-stuffs it is not so easy to support the corresponding assumption, because one cannot unconditionally compare the dyeings given by Patent blue—which draws badly—with those furnished by fast red in which the dye-bath is completely exhausted.

Taking first the case of the developing dyes, in which there is no doubt but that they are retained solely by mechanical adhesion on and in the fibre. The great fastness of many of these dyeings indicates that adhesion is a force sufficient to produce a very intimate union between a dye-stuff and a fibre. If, however, an excess of dye-stuff be used, a porti n is then only imperfectly fixed, and the dyeing will no longer stand rubbing and washing. The cause is evidently a partial superimposition of particles of the dye-stuff. The same also happens in the case of all other dyeings, since they are all liable to lose colour, under the effect of rubbing and washing, when produced by means of an excess of dye. Consequently, adhesion is a property common to all dye-stuffs, and therefore such abnormal phenomena as those already mentioned, where a portion of the dye behaves differently from the rest, should be left out of consideration in studying the dyeing process.

Proceeding further with a comparison of the various dyeings in the finished state, it will be found that they behave almost exactly the same as the dye-stuffs used in their preparation; sublimable dye-stuffs exhibit the same property in their dyeings; and dye-stuffs can be brominated, diazotised, etc., on the fibre just as in their original state. The analogy furnished by comparing the most divergent dyeings is therefore unmistakable.

As regards the nature of the dyeings, there are only two alternative possibilities: either the dye-stuff is present in the free state in the dyeing, or there has been a more or less complete chemical combination on the part of dye-stuff and fibre, and of such a character that the general properties of the former have been retained, as is, for instance, the case with salts.

Hitherto it has been found impossible to arrive at a decision in respect of these possibilities from the investigation of the finished dyeings; but the examination of the means by which dyeing is produced offers greater prospect of success. In the case of substantive dye-stuffs—which are the only kind that can be taken into consideration here—the process goes on as follows:—

The dye is taken up gradually by the fibre—and best in the warm—the operation being complete in a short time, usually within the hour. At the expiration of this period no more of the dye is absorbed, even though the fibre be left in the bath for days. The slower the rate of absorption the greater its power of withstanding the influence of washing when once fixed on the fibre, though this only applies within certain limits. A portion of the dye always remains behind in the bath, this proportion being the greater the larger the amount of water and dye present in relation to the quantity of fibre and the degree of instability—as regards the influence of washing—of the dye itself. The larger the quantity of dye taken up by a fibre, the less is it capable of absorbing a further amount of the same; consequently, the first portions of dye are absorbed more rapidly and with greater energy, and therefore adhere more firmly to the fibre. The latter has a tendency to absorb relatively more dye from dilute than from concentrated solutions; and a light shade of dye is always relatively faster to washing than a darker shade produced by the same dye-stuff. If it be attempted to re-extract absorbed dye from the fibre by means of water, the following characteristic phenomenon is observed, namely, that, with extremely rare exceptions, this removal is incomplete, even when enormous quantities of water are used, thus showing that the dyeing process is by no means an entirely reversible one in the majority of instances.

When several colours are applied to the same fibre, the amount of each finally absorbed is independent of the order in which they come into action. It is therefore immaterial, so far as the final result is concerned whether the several dye-stuffs be applied together or in succession; though it is essential that the same bath be used, that the dyes taken do not precipitate one another from solution, and also that the fibre be immersed in the bath until the absorption of the dye-stuff ceases.

The vat dye-stuffs also behave in a perfectly analogous manner. These conditions have been most extensively described—though by no means completely—in the case of the acid dye-stuffs; and therefore that special dyeing process will now be gone into more fully.

When an animal fibre is dyed in the aqueous solution of an acid dye-stuff, only a very small quantity of the latter is, in general, taken up by the fibre; and this condition does not undergo any great change when the free tinctorial acids are used. It is only on the addition of an acid to the bath that the increased absorption of dye-stuff necessary to fulfil the requirements of practice occurs; and (according to the results of unpublished experiments) the amount of the dye-stuff then absorbed is in direct proportion to the quantity and strength of the added acid, provided the former does not exceed a certain limit. A similar proportionality in the action of acids has been found to exist for colloidal solutions, in which they effect the transformation of the dissolved colloid (the hydrosol) into the precipitated hydrogel. At all events, the primary effect of the addition of acid in these dyeings consists in the liberation of the tinctorial acids, and then in lowering their ionisation.

A further insight into the nature of this dyeing process is afforded on investigating its course in solutions containing the same quantity of one and the same acid. It is then found that the quantity of dye-stuff absorbed is directly dependent on the quantity of the fibrous material and bath used. Time plays only a secondary rôle; and at boiling heat the dyeing is mostly complete by the end of an hour. In many cases the dye-stuff is distributed between the material and the bath, one portion being taken up by the fibre, and the other remaining in the liquid. If the volume of the latter be increased a larger amount of dye-stuff remains in solution, and *vice versa*. The examination of a series of such dyeings, in which, for example, the volume of fibre and bath remain the same, but the amount of the given dye-stuff varies, shows that the value $\frac{\sqrt[x]{Cb}}{Cf}$ in which Cf is the quantity of dye-stuff absorbed and Cb the amount of dye-stuff left behind in the bath, is a constant. The value of x depends on the nature of the dye-stuff and the fibre, and is mostly greater than 1.

This uniform behaviour, the "law of distribution," which was first discovered by the author in indigocarmine dyeings on silk, enables a deeper insight to be gained into the nature of these dyeings.

In the first place, it establishes a kind of analogy between such dyeings and "solutions," on the one hand, and with the adsorption phenomena observed in the case of colloids, on the other. The law is applicable to all these cases, and it must therefore be concluded that such distribution of a substance between two liquids, or between a liquid and a solid body, cannot be a chemical process, since the occurrence of such a regularity as is expressed by the law is accompanied by the condition that the substance which distributes itself in two media in this manner must be present in the same chemical condition in both. The fact that, in the above formula, x is mostly greater than 1, also indicates that textile fibres have a tendency to take up a relatively larger amount of dye-stuff from a dilute solution than from a stronger one.

This behaviour is also observed in all substantive dyeings, even with those to which the law has not yet been experimentally proved applicable, or in which the root index in the above formula equals 1. The law applies only within certain limits of concentration; if stronger solutions be used, deviations occur; and the same happens when extremely dilute solutions are employed in dyeing. Under the last-named conditions there is really no distribution of the dye-stuff between the fibre and the bath, the whole being taken up by the former. On this account, dyeings cannot be regarded as the "solid solutions" assumed by O. N. Witt, because if an aqueous solution of a substance be shaken up with a solvent which is not miscible with water (*e.g.* ether), a distribution of the said substance between the two solvents always takes place. Moreover, other weighty reasons militate against this hypothesis, though for reasons of space, they cannot be gone into more closely.

The aforesaid peculiarity, which is characteristic for substantive dyeings, is also analogous to the adsorption phenomena exhibited by colloids, for, in that case also, a dissolved substance is taken up in relatively greater quantity from dilute solutions than from more concentrated ones. The particles of substance adsorbed by the colloid are retained with great tenacity, and cannot be extracted by means of solvents; just in the same way that it is almost always impracticable to dissolve out the final traces of dye from the dyed fibre. In most cases, therefore, it is quite as impossible to cause the reversion, to the gel condition, of a substance that has been adsorbed by a colloid, as it is to reverse the adsorption of a dye-stuff by the fibre; in the majority of instances both sets of phenomena are only partially reversible.

The more completely a dyeing can be reversed, the more easy is it to decide whether the process goes on in accordance with the law of distribution or not. The examination of picric acid dyeings on silk, and of Patent Blue N and Cyanine B on wool, has, as a matter of fact, proved the applicability of the law to these dyeings as well.

The question now arises whether it is permissible, or not, to claim that this law is generally applicable to the entire group of the acid dye-stuffs. This may be answered in the affirmative, in so far that one may fairly assume that no essential difference exists between the dyeings obtained with acid dye-stuffs, aided by additions of sulphuric acid on the one hand, and of weak organic acids on the other. Moreover, dyeings analogous to the above may be obtained by using a faintly acid bath (acetic acid) in the case also of dye-stuffs that draw completely. In this way it would also be possible to demonstrate the validity of the law in the case of numerous dye-stuffs of the fast red group.

Dyeings with acid dye-stuffs may therefore be classed as adsorption compounds. They cannot be chemical combinations of dye-stuff and fibre; because, the law of distribution would not then apply; and the widespread view that they represent salts of the fibrous substance and the tinctorial acids is contradicted by the previously mentioned fact that both the quantity and strength of the acid present in the dye bath favour their production, whereas the contrary would be the case in the formation of salts. Furthermore, it has already been stated that they cannot be regarded as solid solutions.

The process of dyeing cotton with substantive and sulphur dyes is so far analogous to the dyeing of wool and silk with acid dye-stuffs that the applicability of the law of distribution to this class of dyeings has also been established. The difference is that, in the case of cotton, the dye salts are taken up, *per se*, by the fibre, whereas with the acid dye-stuffs it is only the tinctorial acids that are absorbed.

In dyeing basic dye-stuffs on animal fibres, or on cotton prepared with tannin and tartar emetic, only the colour bases of the dye-stuffs are taken up by the fibre. E. Knecht, who was the first to discover this fact, founded on it a chemical theory of dyeing, which was at one time adopted by the majority of chemists, and even now has some adherents. According to Knecht, wool and silk possess both acid and basic properties. If they are dyed with a basic dye-stuff, the dye base is fixed by the acid group in the fibre, a salt being formed. Similarly, the formation of a salt is assumed to take place by the combination of the assumed basic groups in these fibres with the tinctorial acid when wool and silk are dyed with acid dye-stuffs.

This theory of salt formation, which cannot explain the above described behaviour of the acid dye-stuffs, also leads to unsolvable contradictions if applied to the process of dyeing with basic dye-stuffs, since this process does not depend on the basicity of the colour bases, and also goes on when the assumed acid groups in wool and silk have been neutralised by mordanting with a substance that would lead to the formation of salts; for example, with alumina. Like the animal fibres, glass and clay are dyed only by the colour bases in basic dye-stuffs—and so forth. Finally, as Walker and Appleyard have shown, the procedure in the production of these dyeings is quite different from the formation of a salt.

The process of dyeing with basic dye-stuffs exhibits, however, all the peculiarities already alluded to as evidenced by all substantive dyeings. In this case also there appears to be a regular distribution of the dye-stuff between the dye bath and the fibre; so that the assumption that these dyeings, too, are adsorption phenomena has much in its favour.

This attempt to consider the processes of dyeing from a common standpoint, does not, of course, complete any explanation of the processes themselves, though it has demonstrated the analogy with the adsorption phenomena observed in the case of colloids. In connection both with these latter and with dyeings there is still a good deal to be cleared up, especially as regards the cause of the phenomena themselves; the insolubilising of a soluble substance as the result of adsorption, etc.

The difficulties which the investigation of these processes presents to the research worker are based on their peculiar nature, which consists in their forming a transition between purely mechanical processes on the one hand and chemical on the other. Van Bemmelen, to whom we are indebted for fundamental work on adsorption phenomena, regards them as the precursor of chemical combination; of course, only in such cases where there is a possibility of chemical combination taking place. Consequently the possibility of a partial chemical fixation of the adsorbed substance cannot be excluded in many adsorption phenomena, and also in the case of dyeings with substantive dye-stuffs.

III. Classification of Dye-Stuffs; Methods of Dyeing.[1]

Since in this chapter we are only concerned with the application of the dye-stuffs in the processes of dyeing and printing, the sole principal of classification we can adopt is based on the method of dyeing necessary to bring them on the fibre. The different classes of dyes, therefore, may be set down as follows:—

1. Acid dye-stuffs.
2. Basic or tannin dyes.
3. Dye-salts or substantive cotton dyes.
4. Mordant dyes.
5. Sulphur dyes.
6. Vat dyes.
7. Developing dyes.
8. Albumin dyes.

1. Application of Acid Dye-Stuffs.

The acid dyes are mostly sodium salts of sulpho acids, and this class comprises the different marks of tropeoline, ponceau, Bordeaux, scarlet, fast red, chromotrope, black azo dyes (such as naphthol black) acid violet, acid green, several aniline blues, patent blue, several fast blues or indulines, tartrazine, sulphonated rhodamines (fast acid violet), alizarine saphirol, quinoline yellow, azo-carmine, indigo carmine, etc., as well as such dyes as owe their acid character to the presence of nitro and hydroxyl groups—the nitro dyes and eosines.

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[1] For details applicable to the separate dyes, the reader is referred to the instructions issued by the various makers of dye-stuffs.

Dyes of this class are more frequently used than any others for dyeing wool and silk, but are not well adapted for dyeing cottons.

Application to Wool.—The dyeing is effected in presence of acids or acid salts, *viz.* sulphuric acid, sodium bisulphate—mostly known as tartar preparation—Glauber salt (sodium sulphate), alum, acetic acid, ammonium acetate, or ammonium oxalate. Of these, sulphuric acid and acetic acid are the most frequently used; and of late, formic acid, which has an intensive and uniform action, has also been employed. The object of these acid adjuncts is to neutralise the calcium bicarbonate in the dye water, liberate the dye acid, and drive it on to the fibre. The stronger the acid, and—up to a certain point—the larger the amount, the better and more quickly is the dye absorbed by the wool.

An equally important rôle is played by Glauber salt, which acts as a regulator to ensure uniform absorption of the dye by checking the rate of absorption. This it does by bringing the dye acid into solution as a sodium salt. The selection of the adjuncts to the bath depends, therefore, primarily on the equalising properties of the dyes used and their tendency to draw well or badly, as the case may be.

In addition, it has to be considered whether the dye in question will stand a strongly acid bath or not; and another important factor influencing the selection of the adjunct is the quality of the goods to be dyed, closely woven goods being harder for the dye to penetrate uniformly than is the case with slack-twisted yarns. In the former case the operation must therefore be allowed to proceed slowly, and in a faintly acid bath.

Another factor regulating the absorption of dye is the temperature, the rate increasing as the latter ascends. Therefore, since high acidity of the bath and high temperatures accelerate the absorption of the dye, whilst Glauber salt has a restraining action, it is necessary, in the case of dyes that do not equalise well and goods that are hard to dye through, to commence operations at a low temperature and in a faintly acid bath containing dye-stuff and Glauber salt only, the necessary acid being added in several portions at a later stage. The various fast reds are best dyed in this way.

With a dye that equalises readily it is possible to start with a very—sometimes boiling—hot, strongly acid bath, provided, of course, that the dye-stuff itself will stand a very strong acid bath. In some difficult cases the bath is allowed to become gradually acid during the operation, by adding ammonium acetate or oxalate, these salts being slowly decomposed, with liberation of ammonia, on heating.

The usual method of dyeing wool with acid dyes is as follows: The bath is charged with 2 to 4 per cent. of sulphuric acid, 10 per cent. of Glauber salt, and the (filtered) solution of dye-stuff, the goods being entered at lukewarm or medium temperature and gradually raised to boiling, which is maintained for one hour to one and a quarter. This prolonged boiling is essential for securing the equalisation of the dye, though some dyes, such as indigo-carmine, dye well at somewhat lower temperatures. Only in the case of light shades is three-quarters of an hour's boiling sufficient; and here it is advisable, in the interest of better equalisation, to dye with less acid and more Glauber salt.

The foregoing method is applicable to the majority of dyes, and an addition of 1½ to 2½ per cent. of sulphuric acid will generally be sufficient; naturally this is also influenced by the hardness of the water.

In the case of dyes that equalise well, *e.g.* quinoline yellow, naphthol yellow, patent blue, cyanol, fast acid violet 10 B., fast green (bluish), azo-carmine, chromotrope 2 R., etc., the goods are entered direct into the boiling bath. On the other hand, with a large number of dyes inferior in this respect, such as the ponceaus, scarlets, fast reds, Bordeaux, etc., the goods are entered at medium temperature, and an increased addition of Glauber salt—about 20 per cent.—is very desirable, though not absolutely necessary. In such cases it is usual in practice to useabout 10 per cent. of Glauber salt and 10 to 15 per cent. of sodium bisulphate. With regard to the latter, which is also used alone, it is frequently contaminated with saltpetre, which may do harm in dyeing, owing to the liberation of nitric acid. Ten parts of the bisulphate may be replaced by 4 of sulphuric acid and 10 parts of Glauber salt.

The black acid dyes are mostly used in association with bisulphate, though a better plan is to commence dyeing with Glauber salt and acetic acid, a small percentage of H_2SO_4 being afterwards added to help to draw the dye. Some of them can be dyed without Glauber salt, *e.g.* naphthyl aniline black 4 B with acetic acid, followed by sulphuric acid; naphthylamine M with oxalic and acetic acids, etc.

In the most difficult cases of all, where the dyes equalise badly and the stuff is hard to dye through, the material is first dyed, with or without Glauber salt, and then treated with an addition of acetic acid or an ammonium salt.

The eosines require to be dyed in a faintly acid bath, one of the following methods being pursued: (1) The bath receives an addition of 2 to 10 per cent. of acetic acid (or alum) according to the hardness of the water and the intensity of the dyeing; (2) the goods to be dyed are first boiled in a bath containing 5 per cent. of alum, 5 per cent. of acetic acid, and 5 per cent. of potassium bitartrate, the solution of the dye-stuff being added after the bath has been cooled down to 50° C. The temperature is afterwards again raised to boiling-heat. This second method gives the more brilliant dyeings. In either case less boiling is required than with the other acid dyes, a quarter of an hour to half an hour being sufficient.

For combination dyeings, the selected dye-stuffs should be similar in their behaviour during the process, the choice therefore generally falling on such as equalise well and are able to stand a strongly acid bath.

Shading off is effected at boiling-heat in the case of dyes that equalise well; in other cases the bath must first be cooled by an addition of cold water.

Dyeings that have come out too dark or patchy may be corrected by a treatment with hot soda solution.

Finally, it may be mentioned that dyes generally equalise better in old bath liquors, *i.e.* such as have already been used several times over. The cause of this is of a two-fold character; in the first place, the bath contains a larger quantity of Glauber salt (from previous dyeings); and secondly, the repeated boiling of different parcels of wool has extracted a larger amount of wool substance, which, like the bast of silk, helps to retard the absorption of the dye.

An older method, used with acid dyes, especially scarlets, consisted in dyeing with a small percentage of stannous chloride and potassium bitartrate, or with oxalic acid with or without addition of a tin salt. The resulting dyeings are brighter and mostly also faster to milling than those obtained by the aid of Glauber salt and sulphuric acid.

The alkali blues, which also belong to the acid class of dyes, are dyed in a special manner, owing to the fact that the corresponding dye acids are insoluble in acidified water. The goods are first entered in an alkaline bath (boiled for three-quarters of an hour to an hour) wherein the wool takes up the dye in a colourless form. Borax is the most suitable alkali for this purpose, 5 to 10 per cent. being used; soda (1 to 2 per cent.), though sometimes employed, is disadvantageous for the fibre on account of its strong alkalinity. After this preliminary treatment the wool must be very thoroughly washed, and is then entered for about twenty minutes in a second bath, containing 5 per cent. of sulphuric acid. Here the colour is developed, coming out greener in shade, it may be stated, in proportion as the developing bath is cooler. If greater milling fastness is desired, the colour is developed with alum instead of sulphuric acid.

These alkali blue dyeings, which unfortunately are of only very low fastness to alkali and light, are, however, characterised by good milling fastness (provided they are well washed after the first bath) and considerable beauty. Shading, when desired, is effected by means of acid dyes applied in the second (acid) bath. Dyeing to pattern is a more difficult operation with these dyes, owing to the fact that the colour is only developed in the second bath.

Application to Silk.—Here also, and for the same reasons as in the case of wool, the dyeing is performed in an acid bath, sulphuric acid being most generally used. In some cases—eosines, for instance—such a strong acid bath is unfavourable, and should be replaced by acetic acid or tartaric acid. The silk draws the dye even in the cold, and—just as in the case of wool—it is possible to accelerate or retard the absorption to suit the equalising powers of the dye by regulating the temperature, degree of acidity, and the use of more or less bast soap, which here replaces Glauber salt. Instead of bast soap, a 2½ per cent. solution of Marseilles (olive oil) soap and a 0·4 per cent. solution of gelatine may be used at least for dyeing on the small scale.

The acidified bast soap bath is prepared by boiling with the required quantity of acid; the silk is entered and then lifted, and then only is the necessary quantity of water added, along with a portion of the dissolved dye. In this method the fat separated from the bast soap remains in a state of very finely divided emulsion, which is not the case when the whole of the water and acid are added together. According to the equalising power of the dye, the amount of bast soap solution taken ranges from one-third to one-fourth of the entire bath, one-third part of bast soap solution and two-thirds water being generally used for starting. A larger proportion of bast soap is used when uneven dyeing is anticipated or when the silk has acquired a dusty appearance, due to defective treatment in process of weighting with sodium silicate.

The dissolved dye is added by degrees during the operation. The silk is entered at 30° to 40° C., well worked about whilst the temperature is being raised to near boiling-point, and is finished at a temperature of about 90° C. Actual boiling-heat should be carefully avoided. In the case of the eosines brighter colours are obtained at temperatures somewhat lower than the foregoing. Raw silk must be dyed lukewarm, souple silk at a lower temperature than fully scoured silk. Very delicate colours, being dulled by sericin, must be dyed without bast soap.

After dyeing, the silk is washed, then livened or brightened by treatment in a lukewarm to hot bath (more or less strongly acidified by the same acid[1] that was used for dyeing), and is afterwards drained and dried without rinsing. This treatment brightens the colour and improves the feel of the silk, *i.e.* makes it more brittle and harder to the touch, as well as giving out a crunching sound when compressed. The degree of "feel" produced is varied according to the purpose for which the silk is intended, and is the greater in proportion as the bath is hotter and more strongly acid. To remove the feel entirely, the silk is immersed for several hours in a lukewarm bath containing 25 to 30 per cent. of fuller's-earth, calculated on the weight of the silk; the same softening effect is also obtained by treatment with the so called "two oils" (see under Oleic Acid). The goods so treated are employed for producing a "moiré" finish, silk with scroop being unsuitable for this purpose.

Shading with another dye is sometimes practised in the brightening bath. In order to obtain fastness to washing, the dyed goods are put through a solidifying treatment (*q.v.*).

Dyeings that have come out too dark or patchy are corrected in a bath very rich in bast soap, which extracts part of the dye.

As in the case of wool, the alkali blues are first applied in an alkaline bath, and the colour developed in an acid bath. The first bath is charged with 10 to 15 per cent. of Marseilles soap for light shades, or 20 to 30 per cent. for dark shades, together with the requisite amount of dye, the silk being entered hot and finished by boiling. It is next well washed—otherwise the colours will come out dirty—and the colour is developed in a bath containing sulphuric acid; stannous chloride and hydrochloric acid being used instead when greater fastness is desired.

Application to Cotton.—The acid dyes are not well adapted for dyeing cotton, their affinity for cellulose being almost *nil.* Nevertheless they have been used for this purpose in the absence of more suitable dyes—previous to the introduction of Congo red—and are still, though only to a limited extent, *viz.* for the production of a vivid scarlet by means of croceines and similar azo dyes. The *modus operandi* is as follows: The cotton is first steeped for some time in a fairly concentrated solution of basic alum, and then dyed in a lukewarm dye-bath containing a minimum of water; or else the dyeing is effected in a single bath containing an addition of alum and common salt. Brighter colours are, however, obtained when the cotton is first treated with a cold (about 4° B.) solution of sodium stannate, for one to one and a half hours, previous to the alum bath. The eosines also can be applied to cotton in a lukewarm bath with a large proportion of common salt. All these dyeings, however, are so poorly fixed that they must not even be rinsed afterwards.

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[1] A few grammes of acid per litre (parts per mil.). Sulphuric, tartaric, citric, formic, and acetic acids are used according to the colour and "feel". Of late, formic acid is largely used in place of sulphuric.

Some acid dyes, *e.g.* marine blue, produced by sulphonating strongly basic dyes, can be applied to cotton after the manner of the basic dyes, *i.e.* subsequent to the treatment of the material with tannin. (See later.)

2. Application of the Basic Dye-Stuffs.

The basic dyes are mostly salts of colour bases with hydrochloric acid or with zinc chloride. To this class belong several azo dyes, such as chrysoidine and Bismarck brown, also auramine, the rosaniline dyes, and such of the malachite green series as are not sulphonated, the rhodamines and pyronines, acridine dyes, methylene blue, most of the oxazines, such as new blue and Nile blue, the safranines, indones, eurhodines; finally, also the indulines and nigrosines, in so far as they are not sulphonated compounds. The use of these dyes is chiefly for dyeing and printing cotton. They are dissolved in distilled water with addition of a little acetic acid. Auramine alone is dissolved in neutral water (not too hot). Only filtered solutions are used for dyeing.

Application to Wool.—Wool takes up the basic dyes in a very uniform manner, without the use of any adjuncts in the dye-bath, and the absorption begins at a temperature of 30 to 40° C. Hard water should be corrected with acetic acid until the reaction is slightly acid, since otherwise the colour bases separate in resinous masses and cause streakiness, which is impossible of removal. A slight addition of acid is also desirable, because the wool mostly retains some alkali from the washing process, and this, by forming the colourless colour base, would retard the absorption of the dye. Moreover, these dyes draw more slowly in a faintly acid bath, a condition recognised as favourable in dyeing operations generally. Too much acid hinders the absorption of the dye. The goods are entered lukewarm, and the operation is continued for about an hour, the temperature not being allowed to exceed about 80° C. Dyeings performed at boiling-heat are less brilliant in colour. Nevertheless, gentle boiling is admissible in the case of dark shades, and of a few dyes of this class, such as methyl-violet. Auramine must be dyed in a neutral bath.

The brightest colours are obtained by adding a little Marseilles soap to the neutral dye-bath, and avoiding higher temperatures, about 50° C. being the limit. In this case, however, in order to avoid stains, the water must first be boiled with soap, and the resulting scum removed. This method is very seldom used in practice.

The necessary quantity of wool is added in two or three portions during the operation, and not all at once. Wool that has been sulphured is not, as a rule, fit for dyeing with basic dyes.

As far as possible the combination of basic dyes with those of acid character should be avoided, since in many cases it leads to the formation of insoluble precipitates which may produce spotting. Frequently, however, basic dyes are used for topping dyeings produced from other groups of dyes, the object of this treatment being to shade or enliven the colours. The operation is generally performed in a fresh bath.

A very special process is employed for dyeing with many of the green dyes, such as brilliant green, methyl green, malachite green, etc. The wool is entered in a boiling hot bath of sodium hyposulphite, sulphuric acid, and alum, in a wooden vat, and is worked about in this bath for three-quarters of an hour after steam has been shut off; it is then drained in the hydro-extractor, rinsed, and dyed at about 50° C. in a bath containing about 3 per cent. of acetic acid, in addition to the dye. The bath liquors should be kept for use over again; the oftener they are used the finer the colours obtained.

In the above process sulphur is precipitated on the fibre, and assists in fixing the dye. These dyes can, however, be applied in a simpler manner by passing the wool through a hot soap bath (1 to 2 per cent. of soap), and then dyeing in a fresh, luke-warm dye-bath. This method is seldom used, though occasionally resorted to for the production of a brilliant green of greater fastness than is afforded by the use of the various acid greens.

Basic dyeings on wool are characterised by lustre, good equalisation, fastness towards alkalis, and milling fastness. They are, however, fugitive to light, rub off under friction, and bleed into any adjacent undyed portions when washed.

Application to Silk.—The basic dyes are rapidly taken up by silk, even in the cold. The process is conducted at temperatures up to about 50° C. in presence of acid dyes, and at higher temperatures in a bast soap bath slightly qualified with acetic acid or tartaric acid, the dye being added in several portions during the operation.

These dyes play only a small part in silk-dyeing. The most generally used members of the group are rhodamine, methyl violet, malachite green, Magdala red, and fuchsine.

Application to Cotton.—This is the main sphere of usefulness of the basic dyes. They dye cotton direct, producing very handsome light shades, which, however, cannot be utilised in practice, owing to their fugitive character. Only in the case of several soluble indulines, such as indamine, methylene grey, etc., can somewhat more stable dyeings be produced by the aid of alum, provided a medium temperature be not exceeded.

It must not, however, be forgotten that a variety of dyeings can be produced with basic dyes, on cotton that is to be spun into half-wool vicuna yarns, by the aid of alum and medium temperatures. The fastness of the dye is improved by entering the cotton first in a hot soap bath, then in a cold bath of stannous chloride, and finally in the dye-bath. In some cases the cotton is first steeped for a short time in a solution of basic alum then treated in a chalk bath, followed by a weak tannin bath, and finally by the dye-bath proper. In this manner, methylene blue, for example, will furnish purer blue dyeings than when fixed with tannin and antimony.

The only rational method of dyeing cotton with basic dye-stuffs consists in first preparing the material with tannin or a fatty acid salt of alumina, and then dyeing by gradually heating the bath to about 60° C. during half an hour or an hour. Some dyers prefer to dye without heat, since brighter colours are then obtained; these, however, are not so well fixed as those furnished by the hot process, and consequently the method is only advisable for light and medium shades. In a few instances, *e.g.* indoine blue and several fast blues, the dye-bath must be heated to boiling.

The fact that basic dye-stuffs can also be dyed in a single bath and fixed with tannin, has already been mentioned in dealing with mordanting.

Dyeings performed on cotton prepared with tannin are faster, but less handsome, than those obtained with the aid of fatty acids. A remarkable example of this is afforded by the rhodamines, a dull lilac being produced by tannin, whereas fatty acids give a handsome rose-red.

As already mentioned in the case of wool, hard water should be corrected before use for dyeing basic dyes; and here also an addition of acetic acid is essential when light shades or badly equalising dyes are in question. Some of the latter, *e.g.* those used to imitate indigo dyeings, *viz.* induline, indoine blue, etc., must receive an addition of alum, since otherwise uniform dyeing will be a result difficult of attainment.

In many instances the goods dyed with basic dyes are put through a supplementary treatment; some colours, *e.g.* fuchsine, are brightened by a treatment with hot alum solution; others are rendered faster by passing the goods through a bath of tannin. Finally the fastness of the above-mentioned blue dyes is improved by a supplementary treatment with potassium bichromate, this "after-chroming" being effected by treating the goods for some time in a solution of the salt in question (1 per cent. for dark colours) at a temperature of 30° to 60° C.

To increase the fastness of these dyeings to light, it has been proposed to treat them with zinc polyglycosate, or with a mixture of a copper salt and glucose.

Thanks to their great affinity for the fibre, the basic dyes may also be used for shading and topping cottons that have been dyed with dyes belonging to other groups.

3. Application of the Direct or Substantive Cotton Dyes.

To this group belong the benzidine, diamine, and Congo dyes, their principal employment being in the direct dyeing of cotton. Their introduction produced a revolution in the cotton-dyeing industry, the simplicity and cheapness of the process, and the non-necessity for using tannin or mordants, quickly raising these dyes to a position of high importance, though of late years they have largely been displaced by the sulphur dyes. Moreover, they are surpassed in brilliance by the basic dyes and in fastness by the adjective dyes; they are likewise more susceptible than the basic dyes to impurities in the material and to injury during the gassing process—on which account they should be gassed in a plate machine and in a moist condition. Some of the dyes of this class, *e.g.* cloth brown, anthracene red, carbazol yellow, the sulphone dyes, etc., are more suitable for wool-dyeing than for cotton.

The subject of these dyes has been treated in an excellent manner by A. Kertesz, in a book issued by L. Cassells & Co.

Application to Cotton.—The adjuncts used in the dye-bath comprise common salt, Glauber salt, soda, potash, sodium phosphate, and soap. The two first-named help to precipitate the dye, and therefore accelerate absorption, whilst the others, being alkaline, exert a solvent action and therefore retard the process.

Here, therefore, just as in the case of dyeing animal fibres with acid dyes, we have the means of controlling the rate of absorption, in accordance with the equalising power and drawing of the dye, and the quality of the material to be dyed. Of the foregoing adjuncts, common salt, Glauber salt, and soap alone are used by themselves, the others being always employed in combination.

Common salt or Glauber salt can be used singly for dyeing any of the members of this group of dye-stuffs, though in practice they are confined to the slow-drawing dyes.

Some dye-stuffs which will not stand acid are dyed with soda alone, and are not rinsed afterwards, *i.e.* the alkali is intentionally allowed to remain on the fibre in order to counteract any subsequent exposure to acid. In the case of substantive dyes that are difficult to equalise it is often best to employ soda as the sole addition.

In most instances, and in all combination dyeings, an alkaline reagent retarding the absorption of the dye, and a precipitant, are used in conjunction. When it is necessary to reduce the rate of absorption, as is the case with light shades and stuffs that are difficult to dye through, the alkaline reagent alone is added at the outset, the precipitant being added at the end of about half an hour; were it not for this latter, too much of the dye would be left behind in the bath. This method is also recommended for dyeing mixed shades.

Soap is preferably employed for light shades or difficult mixed colours, and it has also the advantage of softening the material in yarn-dyeing. In all other instances, soda is generally preferable to soap as the alkaline adjunct; the latter smears the dye vats.

As a general thing, the yellow dyes are applied in a neutral bath, the blues in a neutral or alkaline bath, and the reds in a strongly alkaline bath. Some dyeings—mainly yellows and some reds—come out brighter when sodium phosphate has been added; and in many red dyeings the same effect follows the use of Turkey-red oil. This addition is also to be recommended when equalising presents difficulties, especially in dyeing yarns, the Turkey-red oil (or monopol soap) facilitating the damping of the cotton and the uniform absorption of the dye.

The usual adjuncts are employed in the following proportions and with the following dye-stuffs:—

1. Common salt or (calcined) Glauber salt. These are chiefly used for slow-drawing dyes and dark shades, the proportions taken being 10 to 15 per cent. for light shades, and 20 to 30 per cent. for dark shades, calculated on the weight of the cotton. In a few cases (Mikado dyes, Nyanza and Tabora blacks, etc.) as much as 50 to 100 per cent. or even more is taken. This

adjunct is suitable for the Mikado and Hessian dyes, for primuline, diamine golden yellow, Titan rose-red, diamine green, various cotton browns, benzo grey, etc. For the most part, purity is not an essential feature in these salts, ordinary Glauber salt and rock salt being quite suitable for the purpose, except in the production of delicate light colours, for which crystallised Glauber salt or ordinary common salt should be used.

2. Soda and Glauber salt. For dark shades, 5 per cent. of soda and 15 per cent. of Glauber salt are taken, the quantities being reduced to one-third in the case of light shades.

This method is applicable to nearly all these dyes, especially for most of the diamines, Chicago and Zambesi blues, many mixed shades, etc.

3. A mixture of 5 per cent. of potash and 2 per cent. of soap is frequently used for dark shades of the various red dyes of this group—Congo, benzopurpurine, etc. as also for several blues, *e.g.* benzo-black blue. The highly important benzopurpurines, however, give fuller shades with sodium phosphate and soap, and brighter colours with sodium silicate and soap.

4. With 10 per cent. of sodium phosphate and 2 per cent. of soap (for dark shades) advantageous results can be secured in dyeing many yellow shades, such as chrysamine, chrysophenine, thioflavine S., thiazol yellow, Congo and toluylene orange, as well as others, such as benzazurine, Congo-corinth, and many mixed shades.

5. Caustic soda is used only in dyeing with the Trona dye-stuffs, such as Trona red, St. Denis red, etc., the bath being prepared with 100 to 150 per cent. of common salt, and the dye-stuff being dissolved in caustic soda (3 parts of alkali to 4 parts of dye-stuff).

When a number of substantive cotton dyes are used together for the production of mixtures, it is advisable to select such as are of similar behaviour. The adjuncts used will then depend on the properties of the predominating components of the mixture; and in these cases soda and Glauber salt, or soap and sodium phosphate, will be used almost exclusively.

The chief point to be considered in the selection of the adjuncts is the drawing property of the dye; and the influence of the adjunct on the shade of the colour must not be overlooked. Thus, for example, diamine green is dulled by alkalis, and must therefore be dyed in a neutral, or, at most, faintly alkaline bath.

As regards the temperature to be maintained in dyeing with this group, the following observations apply: For light shades the goods are entered at 30° to 40° C., and the bath gradually heated to 50° to 60°, the dyeing process occupying about half to three-quarters of an hour.

For medium and dark shades the initial temperature is 50° to 60° C., the bath being then slowly raised to boiling-point and kept thereat for about an hour. For deep shades, however, it is generally preferable to boil for only three-quarters of an hour at first, then shut off the steam and leave the goods to draw for about half an hour. They must not, however, be left too long in the slowly cooling bath, or red patches of precipitated dye will be formed.

The quantity of bath water plays an important part in the dyeing with substantive cotton dyes. Most of them draw badly, and consequently it is necessary to work with a minimum of water when dyeing dark shades. The maximum quantity of water is 20 to 25 times the weight of the cotton; for dyeing piece goods in the jigger (*q.v.*) a 5 to 6-fold quantity of water will be sufficient; and in machine dyeing still less water is used, though for light shades—especially on mercerised goods—very dilute baths are employed.

With dark shades a portion of the dye will remain behind in the bath, which should, consequently, be preserved. When using these over again, a correspondingly smaller quantity of dye is added, together with only about a quarter the original amount of the adjunct used. In using up an old bath previously employed for the production of a mixture, and therefore containing a number of dye-stuffs, it must not be forgotten that, in consequence of the varying drawing power of the constituent dyes, their proportion will be different from what it was at the outset. Hence, in order to ascertain what proportions of fresh dyes should be added, it will be necessary to make a trial dyeing with the bath as it is, the appearance of the resulting colour giving the requisite information.

The bath is prepared by adding to the water an amount of soda proportionate to the lime content, then boiling up the water with the dissolved dye-stuff, and afterwards running in the necessary quantity of the adjunct required.

After dyeing, the goods are washed, except in the case of light shades produced in a neutral bath. This washing must be performed with particular thoroughness in the case of the blues dyed in strongly alkaline baths, since otherwise the colours will be too dull. The goods must be dried at a moderate temperature, and in a plentiful supply of air, otherwise (especially in the case of benzazurine, Congo-corinth, etc.) irregularities may appear. These may, however, for the most part be prevented by rinsing in salt water after dyeing.

Reds are frequently livened up by means of Turkey-red oil, the goods being passed through an emulsion of the oil, and afterwards centrifugalised and dried.

Cottons dyed with Tiona dye-stuffs are entered into a cold bath of dilute sulphuric acid (1 per cent. strength), without previous rinsing, and are washed afterwards.

In dyeing mercerised cottons the foregoing procedure must be modified in order that the absorption of the dye may take place gradually. Otherwise, the great affinity of the dye-stuffs for the mercerised fibre may easily lead to irregular dyeing. The amount of Glauber salt must therefore be reduced and the temperature raised more carefully, more dilute baths being used, especially for light shades.

Dyes Diazotised and Developed on the Fibre; so-called Ingrain Dyes.—The cotton is first dyed with a substantive dye containing a free amido group, capable of diazotisation, the absorbed dye being then diazotised by treatment in a bath containing sodium nitrite, and finally treated in a developing bath, a phenol, or an amine, to convert the dye into a complex azo compound.

This method was first applied to primuline, and subsequently extended to diamine black, diazo black, etc., and at the present time plays a very important practical rôle.

The dyeings produced in this manner are deeper and faster to washing, many of them also faster to light, than those produced in the first bath without any further treatment. In addition, the diazotisation and development of the colour are accompanied by an entire modification of tone—primuline, for instance, when dyed direct with common salt, giving a yellow, which, though pure, is too unstable to be of any practical value; whereas when diazotised and developed with β-naphthol, it furnishes a red; with ethyl-β-naphthylamine (Bordeaux developer), a Bordeaux: both distinguished for washing fastness, and far superior to primuline yellow in point of fastness to light. The different diamine blacks furnish a grey and a blue, which are also used *per se*. To produce darker shades of greater washing fastness, the dyes are mostly diazotised—with phenylenediamine, or toluylenediamine, for black; with β-naphthol for dark blue, and with naphthylamine ether for lighter and more brilliant blue. Diazo brilliant black gives a Bordeaux shade, which is converted, by diazotisation, into greyish-blue, with β-naphthol, and into brown with phenylenediamine.

A modification of this method consists in developing the diazotised dye with soda, thus producing, not a complex diazo dye, but probably merely replacing the diazotised amido group by hydroxyl. This method chiefly serves for the production of bright browns with the assistance of diamine-catechu, diazo brilliant black, etc., these dyeings being intended to replace catechu. It is also applied to primuline.

The processes of diazotisation and development on the fibre are therefore mainly employed for the production of dark blues, browns, and blacks, also for red and Bordeaux (with primuline).

The *modus operandi* is as follows: The cotton is first dyed with the requisite dye-stuff, then well washed and drained, and afterwards entered in the diazotising bath. This contains 2½ per cent. of sodium nitrite and 7½ per cent. of 20° B. hydrochloric acid for dark shades, or 1½ per cent. of sodium nitrite and 5 per cent. of 20° B. HCl for light shades, and is prepared by stirring the dissolved nitrite, and afterwards the (diluted) hydrochloric acid, slowly into a sufficient quantity of water—which depends on the weight of cotton to be treated—in a with the bath as it is, the appearance of the resulting colour giving the requisite information.

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amount of dye, at the ordinary temperature. The statement, often found in the literature of the subject, to the effect that the fixation of the basic dyes is a special faculty of the substantive cotton dyes, is erroneous, since all dyeings on cotton—indigo blue, alizarine colours, manganese bistre, etc.—possess the property of absorbing basic dyes or their colour bases.

Fixing Substantive Cotton Dyes by Subsequent Treatment with Metallic Salts.—In many instances the fastness to washing or light (or both) of substantive cotton dyes may be improved by immersing the dyed goods in hot solutions of metallic salts. Unfortunately, however, this treatment is accompanied by a change of shade, which renders the process unsuitable for general employment. It is advantageously used for blues intended to replace indigo, among which special mention may be made of Cassella's diamine blue RW, which when "coppered" (treated with copper sulphate) approximates very closely to indigo blue.

The method itself was first applied to Bayer & Co.'s benzazurine, which gives greenish shades very fast to light. Chroming improves the resistance to washing.

The salts employed in this treatment are—copper sulphate (for blues only), chromium fluoride, and potassium bichromate, the mode of application being as follows: The dyed cotton is worked about for a quarter to half an hour in a bath containing 3 to 5 per cent. of copper sulphate (according to the depth of the colour) and kept at a temperature of about 80° C. When piece goods are in question, the bath contains 1½ to 3 parts of copper sulphate per 1000.

Copper sulphate and bichromate of potash are the best, because they increase the fastness to light and washing considerably. The method is specially important for browns and blacks, and consists in treating the dyed materials for 10 to 30 minutes in a boiling-hot bath containing 2 to 3 per cent. of copper sulphate and an equal amount of bichromate, acetic acid being added to clarify the liquor.

To improve the fastness to acids, in the case of certain substantive dyes, such as Congo red, the dyeings may be treated in a solution of solidogen. In many cases, formaldehyde improves the resistance to the effects of washing, particularly with browns and blacks, but the fastness to light is thereby impaired.

Finally, treatment with diazotised *p*-nitraniline proves very efficacious in the production of rich bright shades of brown. The dye-stuffs suitable for this treatment are known as benzonitrol or diaminonitrazol dye-stuffs.

Application to Wool. Of late this application of the substantive dyes has begun to receive the attention it deserves.

Mention should first be made of those dyes which, although belonging to the cotton dyes, are yet more suitable for dyeing wool; these include sulphonazurine, brilliant sulphonazurine, sulphonecyanine, fast diamine red, anthracene red, etc. They may all be dyed with 10 per cent of Glauber salt the acid-resisting fast diamine red also with bisulphate and, except the two first-named, all may be fixed with chrome mordants, thus yielding faster colours. This is done either by mordanting in advance, or, in the case of the reds, by after treatment with chromium flouride. (*See* Mordant Dyes.)

The sulphone dyes (Bayer) must not be dyed at boiling-heat, neither is the customary addition of Glauber salt suitable in this case. According to the instructions given by the Elberfeld Farbenfabriken, these dyes must be used with an addition of ammonium acetate, though inequalities readily occur when this salt is used. For light shades and combination dyeings the following procedure has been found suitable: The goods are entered for some little time - about a quarter of an hour in the dye-bath containing a small percentage (5 per cent. for light shades) of soap, after which about 2 per cent. of acetic acid is added by degrees, to facilitate the absorption of the dye, and boiling is then practised for twenty to thirty minutes. In this manner and by combining sulphonecyanine, sulphone brown, and chrysophenine, for example, perfectly uniform drab shades can be readily obtained, which, however, can now be obtained far superior in point of fastness to light by certain acid dyes.

As regards the true cotton dyes, some of these exhibit, in wool-dyeing, properties which seem to render them more suitable for many purposes than the acid dyes. They are dyed at boiling-heat, with an addition of 10 to 20 per cent. of Glauber salt—according to the depth of shade required—and, should more complete extraction be desired, 2 to 3 per cent. of acetic acid can be added as well. Moreover, in contrast to the case of cotton, these dyes draw very well for the most part when applied to wool. With most of them acetic acid is used, but a very suitable adjunct for many of these dyes is 10 per cent. of common salt and ½ per cent. of potash—soda is altogether unsuitable here—better extraction being obtained by this means.

As in the case of cotton, these dyes can be put through an after-treatment with metallic salts.

The red and yellow substantive dyes—*e.g.* Delta purpurine, diamine scarlet, Emin red, chrysophenine, etc.—are the best adapted for wool, the browns and violets least of all. Their superiority over the acid dyes is expressed in their greater power of withstanding milling and sulphuring. Thus, for instance, none of the many ponceau reds is suitable for dyeing loose wool and yarns for producing parti-coloured fabrics, which will have to be milled or require sulphuring in the piece, in order to clean any white that may be present. More on this point will be given in Section IV.

Finally, it may be remarked that the substantive dyes also play an important part in the dyeing of half-wool fabrics (*q.v.*).

The Application of the Substantive Dyes to Silk was long exceedingly restricted, only a few—chrysamine, chrysophenine, Mikado yellow, etc.—being used.

Of late years, however, they have also become important in this connection, and must be specially mentioned, since many of them can be used with great advantage in silk dyeing—such as diamine scarlet, fast diamine red, the dye-stuffs of the chloramine yellow group, and diamine green, particularly in substitution for alizarine dyes which give rise to considerable trouble when used on silk. Various methods of dyeing are practised; light shades being dyed with additions of sodium phosphate or Marseilles soap, and dark shades with Glauber salt and acetic acid; another plan being to dye in a bast soap bath acidified with a little acetic acid. The bath temperature should only be raised by degrees, and, in the case of light shades, should not exceed the heat of the hand. In the interests of fastness it is advisable to soap after dyeing, and then brighten by the usual means.

The dyeings may also be diazotised as in the case of cotton, and developed or treated with metallic salts. Thus, for instance, primuline red is a very good silk dye; and primuline, developed with soda, gives a yellow that can hardly be surpassed. Very fast olive shades, etc., can be obtained by dyeing with primuline and diamine green, and developing with phenol.

The substantive dyes are also of considerable importance in the dyeing of half-silk goods.

Supplementary Remarks.—In addition to the substantive dyes and several basic dyes, there are also a few others possessing the property of dyeing cotton direct. These are—rhodamine S, cachou de Laval, canarine, a few natural dye-stuffs like curcuma, safflower, and Orleans, though none but the two first are now in use for this purpose.

Rhodamine S is dyed at about 40° C. in presence of a small percentage of acetic acid, and furnishes a handsome rose-red.

Cachou de Laval is dyed for about half an hour at first, without any adjuncts, after which time 6 per cent. of soda is added—to soft water, or correspondingly more to hard water—and the operation continued for half an hour longer at about 70° C. By reason of their cheapness and fastness these dyes are still frequently used for bottoming dark colours; they may be shaded by a treatment with metallic salts, iron, chromium, or copper.

4. Application of the Mordant Dyes.

To this class belong a large number of very differently constituted dyes, all of which possess an acid character, and are indebted to the presence of hydroxyl or carboxyl groups for their capacity of forming lakes with mordants.

Their pigmentary character differs considerably in degree. Some of them, formerly entitled "adjective dyes" are such weak pigments that they are incapable of furnishing utilisable colours when used alone, and require to be combined with mordants, with which substances they produce strongly coloured insoluble compounds known as "lakes". To these belong alizarine and the dye-woods. Others, again, are themselves highly coloured, notwithstanding which they cannot be used for dyeing unless in conjunction with mordants; this section includes galleine and many alizarine dyes. Finally, there are a number of acid dyes and substantive dyes that can either be used alone or fixed on the fibre by means of mordants, this sub-group comprising anthracene yellow, carbazol yellow, fast diamine red, brilliant alizarinecyanine 3 G, chromotrope, etc.

It is, however, impossible to draw any strict line of demarcation between these dyes, their divergences being gradual and not fundamental. Only in the case of the first-named adjective dyes is it perhaps feasible to constitute a separate group; and even here there are individual dyes, *e.g.* santal wood, that possess intermediate properties.

One characteristic possessed by all these dyes in common is that of fastness to milling

In dyeing with mordant dyes, the nature of the bath water plays an important part, and therefore the water used must have been corrected with acetic acid, otherwise a partial precipitation of the colour, in the form of lime and magnesia lakes, may occur. In some cases organic impurities have an unfavourable effect, *e.g.* in presence of cochineal or alizarine blue.

Application to Wool.—This is the most important use of mordant dyes, and, in fact, most of them are suitable for this purpose alone.

The methods of fixing that may be employed in this case are varied, and for convenience of treatment will be described in groups:—

1. Dyeing previously Mordanted Wool.—This is an important process in wool-dyeing, and is applicable to all the mordant dyes. The temperature, duration of boiling, and the addition of acetic acid to the bath, all depend on the nature of the dye; and, from this point of view, the mordant dyes may be divided into three classes:—

(*a*) *Alizarine Dyes.*—These require the greatest care in dyeing, and are, for the most part, very susceptible to the influence of impurities in the goods to be dyed. The *modus operandi* is as follows: The mordanted wool is first treated for a quarter of an hour in a cold bath of dye; the temperature is then gradually raised to boiling, in about an hour, and maintained in this condition for one and a half to two and a half hours, the goods being well worked. Should the initial temperature be unduly high, or the heating proceed too rapidly, unequal dyeing may easily result. Only in the case of loose wool is less care necessary, the initial temperature in that case being up to 40° C. The prolonged boiling is necessary to ensure the proper fixing of the dye.

A neutral bath is the most favourable for some of the alizarine dyes—alizarine red, alizarine orange, anthracene brown, and galleine—that come on the market in paste form. In other instances, especially for the powdered alizarine red, alizarine brown, and galleine, which are sodium salts of dye-stuff sulpho-acids, the liberation of the dye acid entails the addition of an excess of acetic acid (750 c.c. of 8° B. acetic acid per kilo—0·082 gal. per lb.—of dye, when the water has been previously corrected). The different marks of alizarine blue, cœruleine, alizarine yellow, etc., require in addition about 2 per cent. of 8° B. acetic acid to facilitate extraction, this addition being made by degrees at intervals during the process.

In mixed shades of different alizarine dyes it will always be possible, by exercising a little care, to work in a weak acetic acid bath, the acid being added gradually and not until the bulk of the dye has been absorbed.

Delicate light colours and materials that are difficult to dye through, such as felt hat bodies, are preferably dyed in a slightly ammoniacal bath at the start; and after boiling has proceeded for some time, the acetic acid is added until the reaction becomes slightly acid.

To shade dyeings made with alizarine dyes, the bath is neutralised with ammonia, the shading dye is added, and after a short time the acetic acid is run in by degrees. This, however, is mostly done with acid dyes that are fast to milling (such as patent blue A), or else with dye-woods.

(*b*) *Dye-Woods.*—These are easier to manipulate than the alizarines.

The mordanted wool may be entered at 50° to 60° C., and the period of boiling may be shorter, an hour and a half being sufficient for dark colours. A neutral bath is employed.

(*c*) *All other mordant dyes* can be dyed by entering the mordanted wool at 40° C., gradually raising the temperature to 100°. and boiling for an hour to an hour and a quarter—longer boiling being only required in the case of chrome blue and chrome violet, for example, in order to complete the formation of the lake. They are all applied in a weak acetic acid bath, the amount of acid (1 to 1¼ per cent. of 8° B. acetic acid) depending on how the dye draws. In some instances, *e.g.* cloth red, or goods that are difficult to dye, a little sodium acetate is added at first, followed by acetic acid.

Dyeings that have a tendency to dust off, *e.g.* logwood black, are often returned to the mordanting bath for a short time, after dyeing, to improve the fixation of the dye. This treatment occasionally induces a slight modification of the shade, alizarine cyanine, for instance, becoming a little bluer and darker.

2. Dyeing in a Single Bath.—This method has the advantage over the previous one of being quicker, simpler, and therefore cheaper, since the mordanting and dyeing are here combined into one operation.

Owing to the total duration of boiling being shorter than in the first-named method—in which the goods are boiled first in the mordanting bath and then in the dye—there is less risk of shrinkage for piece-goods, or of injury to the wool.

Herein, however, resides the drawback of the process, inasmuch as the formation of the lake in the bath results in a loss of both mordant and dye, and in most cases the dyeings are not so full or so well fixed as in the first method. There are three variants of this process:—

(*a*) *Dyeing in a Single Bath containing both the Dye and the Metallic Salts used as Mordants.*—In this case, therefore, the formation of the lake proceeds in the bath itself, and for this reason an acid substance (oxalic acid or potassium bitartrate) must be added, in order that the colour lake may be presented in a soluble form to the fibre. At the same time it is thus evident that this method, which gives the brightest of all the mordanted dyeings, can only be employed when the colour lake is correspondingly soluble. Its chief uses are in the production of cochineal scarlet, dyeing with yellow dye-woods (especially quercitron), and in a few logwood dyeings which will be dealt with more fully later on.

Latterly, also, this method has been applied to dyeing light shades with alizarine dye-stuffs, and the method is of special practical importance for single-bath alizarine dyeings with the aid of chromium fluoride. The bath is charged with the dye and 3 per cent. of chromium fluoride, the damped goods are entered cold, then slowly raised to boiling and maintained there for an hour or an hour and a half. A number of pale blue, grey, and drab shades are produced on worsteds by this means, with or without vat bottoming.

(*b*) *The Deepening Method.*—This is used in the production of a number of drabs and blues by the aid of fustic, santal, madder, logwood, and sumach. The red dye used in the case of light shades is madder, the more powerful pigment, santal-wood, being employed for dark shades. The dyeings, however, are not very fast and the practice has almost been abandoned.

Used alone, without mordants, the above dye-stuffs furnish only light shades; light drab, for example, being obtained by the help of fustic, madder, sumach, and potassium bitartrate. The addition of logwood furnishes greyer tints.

In most cases, however, these dyeings must be darkened by the aid of mordants. Thus, for example, the goods are first dyed with fustic, madder, sumach, and logwood; the dye-bath is then cooled down quickly by an addition of cold water, a little ferrous sulphate is added, and the whole is boiled up again for an hour.

Dark browns are produced by this method in the following manner: The goods are first boiled for about an hour in a bath containing fustic, santal, logwood, and sumach; then cooled as above, treated with copper sulphate, boiled for another hour—and when required to be still darker, cooled again as before, treated with ferrous sulphate and boiled one hour longer.

It is impossible to give further details, the procedure depending entirely on the shade and depth of colour. For dark browns in general, 3 per cent. of copper sulphate and 1 to 10 per cent. of ferrous sulphate are employed; occasionally, for light shades, only a few hundredths to tenths of 1 per cent. of ferrous sulphate are taken, the copper sulphate being omitted altogether. Iron gives darker, copper brighter shades. This method, which requires much practice, played a large part in dyeing piece goods at one time but is now rarely used.

(c) *After-Chroming; Developing with Mordants.*—Many acid dyes and substantive dyes, such as chromotrope, Victoria violet 4 BS and 8 BS, patent blue, cloth red, milling blue (Kalle & Co.), flavazol (Berliner Actiengesellschaft), anthracene yellow, anthracite black, fast diamine red, anthracene red, etc., can be improved in point of fastness to milling by a hot after-treatment with mordants. This treatment has been styled "after-chroming," because only chrome mordants, *i.e.* chromium fluoride or potassium bichromate, are used.

It has also been found that most of the mordant dye-stuffs (such as diamond black F, alizarine black, anthracene chrome black, etc.) which, formerly, were fixable only by the first-named method, can now be fixed on wool to great advantage, by dyeing and after-chroming; so that the process now occupies a prominent place in the fast dyeings of woollens.

In the case of acid dyes the advantages of this method are, that the fastness of the dyes, particularly with regard to milling, is greatly improved, whilst with the mordant dyes better equalisation and more thorough permeation of the material are ensured with less injury to the wool through boiling.

The after-treatment with chrome mordants renders the colours somewhat darker, but otherwise their appearance undergoes little alteration as a rule. In the case of Victoria violet, purer blues are obtained; but with the chromotropes, to which this method was first applied, a complete change of colour ensues, the red shades produced in an acid bath being converted by this treatment into dark blue to black.

The same applies to the importance of amino-phenolazo dyestuffs and certain acid alizarine dyes, in which case, however, a difference exists in comparison with the chromotropes, inasmuch as the practically useful colour is produced only on treatment with potassium bichromate.

The chemical reaction proceeding in the after-chroming treatment consists chiefly in the formation of a chrome lake of the corresponding dye; in a few instances, especially with several chromotropes (F.B., S), chrome brown and chromogene I. (M. L. Br.) the reaction is one of oxidation, and consequently potassium bichromate is the only means that can be employed for after-chroming these dyes; in other instances the operation is performed partly with chromium fluoride and partly with bichromate. Some dyes, like the aforesaid Victoria violet, are decomposed by bichromate, and must therefore be treated with chromium fluoride. For all others, preference is given to whichever of these two chrome mordants furnishes the best results, chromium fluoride being most frequently selected, since it also renders the wool less harsh than the bichromate.

For the acid dyes the following method is employed. The goods are dyed first in an acid bath as usual, after which chromium fluoride is added—in the proportion of 3 to 4 per cent. for dark shades, or less for light shades—and the bath is boiled for half an hour to an hour longer. When bichromate is used the bath must be first cooled down by adding cold water, and in this case also an addition of a little oxalic acid towards the end of the operation is usually beneficial.

Shading can be effected in the same bath, either before or after chroming, dyes of good equalising power being preferably used. When bichromate has been employed, the shading dyes selected must be such as are able to resist the action of this reagent, *e.g.* patent blue, many acid violets, azoflavine, orange IV, fast acid violet A2R, etc. Darkening with dye-woods, *e.g.* logwood, must be performed in a separate bath.

Mordant dyes, too, are first employed in an acid bath, preferably with addition of sulphuric acid and Glauber salt. In some cases, *e.g.* diamond black, and anthracene chrome black on loose wool or yarn, the Glauber salt is replaced by acetic acid. The amount of acid added depends, of course, on the manner in which the dye "draws," it being necessary to bear in mind that some mordant dyes do not draw so well in presence of a large amount of sulphuric acid as when the quantity of acid is smaller. Generally, a larger amount of Glauber salt than usual will have to be used, or acetic acid employed instead of sulphuric, especially in dealing with heavy, closely woven materials in which the dye equalises with difficulty. In such cases as much as 20 per cent. and more of Glauber salt will be needed.

After dyeing, the bath is cooled down to 50° to 60° C. by cold water, and, after the addition of the chromium fluoride or bichromate, boiled again for an hour to an hour and a half. The quantity of chromium fluoride taken varies from 2 to 6 per cent. and depends on the dye-stuff used; in most instances 3 to 4 per cent. will be sufficient. Bichromate is used in the proportion of 1 to 3 per cent.

Though alum and other mordants can be used for developing, only the above-mentioned chrome mordants are employed in practice. With regard to the choice between the two, the observations already made in dealing with the after-chroming of acid dyes also apply here.

This method of dyeing is of special practical importance for alizarine black, WR (B.A.S.F.) and diamine black (F. Bayer & Co.). For the first of these the method has the advantage of cheapness, whilst by this means the usual difficulty encountered with regard to the equalising of diamine black on mordanted wool is entirely obviated.

Both are dyed in a bath containing acetic acid—first with ammonium acetate and then with acetic acid, in the case of piece-goods difficult to dye through—and afterwards developed in the same bath with 1 to 1½ per cent. of bichromate.

In the case of diamine black, when the goods are not difficult to dye through, Glauber salt is added, together with a little sulphuric acid to ensure more complete extraction; after adding the bichromate the goods are boiled for three-quarters of an hour, or an hour in the case of alizarine black.

With these dye-stuffs the bichromate acts chiefly as an oxidising agent; but how far it also acts as a mordant has not yet been established, since an alizarine black which meets all practical requirements can also be obtained, without bichromate, by steaming the dyeing obtained by steaming the dyeing produced in the acid bath.

Of course, after-chroming can also be carried on in two baths; and in some instances this is advantageous, inasmuch as the two baths can also be used for further dyeings.

Special interest attaches to dyeing with cochineal and a few of the logwood dyeings, which will therefore now be dealt with in detail.

Dyeing with Cochineal.

Cochineal furnishes a red with tin mordants, and an amethyst (bluish-red) with aluminium mordants. The first of these, cochineal scarlet, is one of the oldest, handsomest, and best colours known, and formerly played a very important part in wool-dyeing. Even at the present time the cochineal scarlet shade is highly esteemed, though nowadays it is produced by the aid of various ponceau reds. Nevertheless, when a fast scarlet is required, as is most frequently the case with smooth cloths, it must still be produced by means of cochineal. Frequently the colour is bottomed with cochineal and topped with ponceau, a dyeing of this kind being termed "semi-fast scarlet," whilst the cheaper colour obtained with ponceau alone is called "fugitive scarlet," though the actual difference in fastness between the cochineal and ponceau scarlets is confined to their behaviour during washing and milling, the latter bleeding whereas the former are fast. Cochineal scarlet, however, will not stand treatment with soap or alkalis without undergoing a change of shade and turning a bluish tinge, whilst ponceau scarlet remains free from appreciable alteration. In point of fastness to light the best ponceaus are little inferior to cochineal.

There are two ways of testing the fastness of scarlet—by sulphuric acid and by stannous chloride solution. When touched with the former reagent, a cochineal dyeing gives a pure yellow stain but in the case of ponceaus the colour is more or less brownish. When treated with a solution of stannous chloride of a certain strength—which can be determined by a few tests with the two colours—and heated, the ponceau dyeings are bleached entirely, whilst the cochineal dyeings are less affected. Semi-fast scarlet can also be easily detected by this means.

For the most part, cochineal scarlet is produced with cochineal and lac dye, the resulting colour being somewhat less sensitive to the action of alkalis. In point of fastness to light these two dyes are about on a par; the handsomest shade, however, is that obtained from cochineal alone.

Cochineal requires no preliminary treatment to fit it for use, whereas lac dye must first be mixed into a paste with water, left to stand for several weeks, incorporated with a solution of stannous chloride, and again left for some time, since fresh lac dye will not give a handsome colour, the beauty of the dyeing increasing with the duration of the preparatory treatment. The method of dyeing is the same whether the cochineal is used alone or in conjunction with lac dye; consequently, for the sake of brevity, cochineal alone will be mentioned in describing the process.

Before entering on this description it should be stated that cochineal scarlet may be of various shades—full or thin, and more or less tinged with blue or yellow, as desired. It may be produced by mordanting and subsequent dyeing, or in a single bath. The latter method gives a more handsome red, of yellowish cast, whilst the other method furnished a more intense bluish-red, and the material is dyed through better. Occasionally the two processes are combined, either by adding part of the dye to the mordant bath, or *vice versâ*.

The mordants used are stannous chloride ("tin salt") with oxalic acid, or "acid for scarlet" with potassium bitartrate. By taking a small quantity of tin salt, a dull red, of bluish cast, is obtained, whilst an excess of tin salt or bitartrate gives a yellower scarlet, the latter salt furnishing a handsomer shade than is obtainable with oxalic acid. Scarlet produced with tin salt and oxalic acid is less sensitive to alkalis than that furnished by the other mordant mixture, though, on the other hand, the latter colour undergoes less alteration when heated.

In any case, pure soft water must be used for dyeing scarlet, and the operation must not be too protracted, the colour being rendered muddy by prolonged boiling. It is impossible to obtain a pure scarlet in a copper pan, and tin vessels must therefore be used. Strangely enough, the colour obtained by dyeing in wooden vessels, where there is no metal to cause muddiness, is less handsome than that produced in tin vessels.

The dye should, as far as possible, lie on the surface of the cloth, since in these circumstances the underlying white throws up the colour more brightly. The white section of the dyed goods is a characteristic indication of fast scarlet, the goods being always dyed further through when ponceau has been used.

The best method of procedure to adopt for obtaining a handsome scarlet is as follows: The bath is prepared in a tin vessel, and contains only a part of the necessary cochineal and acid for scarlet, together with (purified semi-crystal) bitartrate. The goods are entered very hot, so as to deposit as much as possible of the scarlet on the surface, the temperature being then raised to boiling, and the rest of the scarlet acid and cochineal added after awhile. The whole operation should not take longer than an hour and a quarter. About 15 per cent. of cochineal is required; but the amount of the mordant cannot be definitely given, owing to its very variable concentration.

Semi-fast scarlets also are produced with cochineal and a ponceau (*e.g.* brilliant cochineal) in a single bath.

In the second method, 3 per cent. of tin salt and an equal quantity of oxalic acid are used.

After dyeing, the goods are rinsed with water, slightly acidified with sulphuric acid to prevent the scarlet being tinged blue by the action of the bicarbonate in the water. The baths are not fully exhausted, and can be used over again with advantage.

By topping the scarlet with rhodamine a very vivid appearance is imparted to the colour. For producing a yellow tinge flavine is generally used, this being added to the cochineal in the dye-bath. Buckthorn berries, and occasionally fustet wood, are also taken for this purpose.

Scarlet occasionally exhibits a number of small black specks, so-called "tin stains" (tin sulphide?), in which event the goods must be steeped in a solution of oxalic acid.

Finally, it may be mentioned that very pale scarlets are also produced for pink shades.

To obtain amethyst shades with cochineal, alum is used, with or without tin mordant. In this case the single bath method is inapplicable on account of the considerable precipitate that would form in the bath owing to the low solubility of the alumina lake. Moreover, lac dye is unsuitable, this dye giving ugly brown shades with alumina mordants. The goods are mordanted with alum, bitartrate and scarlet acid, and dyed in a fresh bath containing a little bitartrate and scarlet acid in addition to the cochineal. It is advisable to add a portion (about 1 per cent.) of the dye to the mordanting bath in order to ensure the goods being dyed through better.

Cochineal dyeings are often darkened by topping with archil; madder or alizarine being also employed for brownish-red tones.

Occasionally the so-called "scouring" process is employed for blueing cochineal dyeings, the dyed goods being treated in a lukewarm bath to which ammonia is added by degrees. The operation must proceed slowly, and the goods must always be somewhat "over-scoured," since the colour goes back a little, *i.e.* loses some of the blue tinge, in drying.

Black and Blue Dyeings with Logwood on Wool.

Logwood is used in the form of chips or as an extract, and occasionally is subjected to a process of oxidation termed "fermentation," the object of which is to convert the hæmatoxylin present in the wood into the true pigment hæmatein.

According to Von Cochenhausen, the different constitution of the chips and extract (which merely contain hæmatoxylin) from that of the fermented product should lead to a modification in their method of employment, which, however, is disregarded in practice. This observer's view is that, in the case of the unfermented wood or extract, the hæmatein is only produced during the operation, either as a result of prolonged boiling or of the oxidising action of the mordant on the hæmatoxylin; consequently these materials should preferably be used, in conjunction with iron and copper mordants, for dyeing wool that has been mordanted with potassium bichromate and sulphuric acid. If, however, the available mordants have no oxidising action, *e.g.* alumina mordants, or potassium bichromate in presence of an organic acid, then better results will be obtained with fermented logwood. Finally, he considers that the fermented product should never be used after the said oxidising mordants, since in such event the destruction of the hæmatein, which is readily oxidised to brown substances, is to be feared.

The fermentation is performed in a primitive manner, usually in the dyeworks, by spreading the logwood chips in irregular heaps, which are then moistened with water, or weak solutions of alkali, and turned over at intervals.

A more rational method of procedure is as follows: The chips are laid in heaps, about eighty inches in depth, on a well-ventilated upper floor, where they are slightly moistened and left for several days or weeks, according to the time of year. The completion of the process may be recognised from the appearance of the wood, which, when properly fermented, is of a dark red-brown colour and exhibits in places (if sufficiently rich in pigment) a greenish incrustation of hæmatein crystals, with metallic lustre. The wood is then spread out in thinner layers and dried at about 50° C. in order to prevent further oxidation, which might prove injurious to the hæmatein.

Logwood extract is prepared in various ways, which may be divided into two chief classes with and without pressure; the former furnishing a larger yield, whilst the latter gives the better quality product. The yield stands in direct relation to the degree of pressure and temperature employed for the extraction.

In extracting under ordinary pressure, which method is adopted in some works, the comminuted and unfermented wood is placed in a diffusion apparatus of the type used in sugar-refining, and is extracted with warm soft water, the sole pressure applied being that of a column of water about 10 feet high. If the product be intended for the calico-printer, the extraction is carried on at 60° C., but if for dyeing, the temperature is increased to 80°. The operation will be finished in about five to six hours, and the residue is used as fuel. Extraction at 80° C. should give a yield of at least 25 per cent.; at lower temperatures it is naturally smaller, but of better quality. If the

American method be employed—extracting in closed vessels—the pressure should never be less than two atmospheres, and the quality suffers in proportion as the yield exceeds 30 per cent.

The solution obtained by one or other of the above methods is clarified by settling, and then concentrated to 30° B. *in vacuo.* The extract for printer's use, which must be entirely free from solid matters, is filtered before concentration, and the latter process is frequently stopped when the density measures 20° B. Solid extract is also made, but is less suitable for use—especially in printing—since in the preparation no trouble is taken to remove impurities, without which latter, indeed, the production of a solid extract by evaporation is impossible. In point of dyeing power, 6 parts of solid extract correspond to about 10 parts of a 30° B. liquid extract.

As regards the quality of the wood to be used, little can be said on this point generally, cheap logwoods being occasionally better adapted for the production of extract than dearer sorts. Extensive use has latterly been made of roots, chiefly from Jamaica, in the production of extract. The very fine extract sold under the name "hæmatein" is prepared from Laguna logwood. A logwood powder is put on the market by Fenerlein of Stuttgart.

The literature on the preparation of logwood extracts is comparatively large, but contains so many unreliable and contradictory reports that it will be left out of consideration here. There are also a large number of patents dealing with improved methods of manufacture and purification. Thus, to give an instance, Foelsing's patent proposes to extract fermented logwood and pass an electric current through the resulting solution kept under pressure, the object of this treatment being to deresinify the extract. With regard to the technical value of this and similar processes no information is available.

Logwood is also extracted by two methods—with and without pressure—in dyeworks. In the latter case the chips are put into bags and boiled in water for two hours in a wooden vat. In the pressure method the chips are put into a small upright boiler and boiled twice—a quarter of an hour each time—with water, under a pressure of at least two atmospheres. A frequent source of error in this method is to work with too large a quantity of chips at a time; properly the boiler should be only about two-thirds full.

The black dyeing of wool with logwood is an art of great antiquity, there having been a guild of black dyers as long ago as the eleventh century. Formerly a fast black was produced on a vat bottoming, but at present, from motives of economy, this method has almost entirely disappeared, leaving the field to the three following processes:—

1. Iron black, or Salzburg black (so called because frequently produced with the aid of "Salzburg vitriol," consisting of ferrous and copper sulphates), with ferrous sulphate and copper sulphate as mordants.

2. Chrome black, with potassium bichromate and copper sulphate as mordants.

3. Single-bath black, mordanted with ferrous sulphate, either alone or in conjunction with copper sulphate.

An important point is the quality of the water used for dyeing, softness being essential; so that hard water must be corrected with acetic acid. The resulting calcium acetate has a favourable influence on logwood dyeings, for reasons that have already been discussed in the chapter on Mordants.

Iron Black is the oldest wool black known; the method is employed in a number of modifications, but only the simplest and most rational form will be described. The material is first mordanted with 10 to 15 per cent. of ferrous sulphate, 4 to 6 per cent. of copper sulphate and 1½ to 2 per cent. sometimes as much as 5 per cent. of potassium bitartrate. Loose wool requires more mordant than piece-goods. In the case of finer goods the proportion of bitartrate is increased, the result being that the material is dyed through better. Dyeing then follows. Nowadays extracts are chiefly used for dyeing loose wool, yarns, and the finer piece-goods, logwood chips serving for lower-class goods. The black obtained by the use of extract is dearer but finer and has a cleaner appearance than that from chips. A very handsome blue-black can be obtained with 10 per cent. of solid extract, the quantity of chips required for dyeing varying between 30 and 60 per cent., according to their richness in dye and the quality of the goods to be treated—the finer the material the larger the amount of dyewood. Some dyers prefer the inferior kinds of logwood (*e.g.* Monte Christo) to the better sorts for this purpose. To convert the bluish tinge characteristic of logwood blacks into deep black, the dye-bath must receive an addition of about 2 per cent. of 30° B. fustic extract. The goods are entered hot, raised to 100°, and boiled for an hour and a half to two hours. After-treatment with copper sulphate is frequently given in order to deepen the black and remedy defective mordanting. When mordanting has been correctly performed the dye-bath will be of a wine-yellow colour. After dyeing, the goods must be thoroughly washed—piece-goods receiving an addition of fuller's-earth—to dissolve the adherent unfixed particles of dye. If this be omitted the colour will rub off to a considerable extent.

Chrome Black.—The production of a deep logwood black with a chrome mordant alone is impossible, this method furnishing a blue-black which, moreover, is fugitive under the influence of light. Consequently, in practice the so-called chrome black is produced with the aid of copper sulphate, the resulting colour being deeper and faster to light; the shade depends on the amount of copper sulphate employed.

The wool is mordanted with 3 per cent. of potassium bichromate, 1½ to 3 per cent. of copper sulphate, and 1½ per cent. of sulphuric acid: and is then dyed in the same way as for iron black. To ensure the black rubbing off as little as possible, which is an important consideration in yarns intended for working up along with white, the wool is returned to the mordanting bath for a short time after leaving the dye-bath.

Single-bath black is produced in two ways. Formerly a common black was obtained by dyeing the goods for some time in a decoction of logwood and 5 to 6 per cent. of sumach, and then darkening with ferrous sulphate.

This, however, rubs off more extensively than any other black dyeing on wool, and its use is therefore restricted to common wools and yarn waste. If a single-bath method appears advisable, either on the score of cheapness or because the prolonged boiling in the two-bath process is likely to injure the quality of the goods, then the dye-bath is prepared with 4 per cent. of ferrous sulphate, 2 per cent. of copper sulphate, 2 per cent. of oxalic acid, 10 per cent. of 30 B. logwood extract, and ½ to 1 per cent. of fast yellow. After boiling the bath liquor and cooling it down with cold water, the goods are entered and boiled for an hour.

An essential condition to success in this method is the use of a proper quantity of oxalic acid, which reagent is added to dissolve a portion of the colour lake formed in the bath, since, like other textile fibres, the wool can only absorb dyes that are presented in the dissolved state.

If the dye-bath contain too little oxalic acid it will seem quite turbid, owing to the greater part of the colour lake remaining undissolved; consequently it will not furnish a full black. On the other hand, if the oxalic acid be in excess, not only will the whole of the colour lake be dissolved, but its absorption will be retarded. In such case the bath is quite pale, and naturally will not give a full black.

A good black can also be obtained with this method by combining logwood with an acid black, such dyeings being naturally faster to milling than those from either of these dye-stuffs singly. However, the single-bath logwood black has now been almost entirely driven out by the acid-dyeing azo dye-stuffs.

The single-bath method is also applicable to other dyeings; thus, a good navy blue can be produced in this manner with logwood, acid violet, and acid green, whilst logwood and cloth red give a fast brown. For this last purpose the single-bath method was first applied, by Oehler, to replace santal; but it has now gone out of use.

Mention may also be made of a single-bath chrome black, which is often dyed on loose wool and yarn. The goods are first mordanted with 1½ to 1¾ per cent. of bichromate and 3 per cent. of (80 per cent.) formic acid until the bath appears free from colour. It is then cooled down quickly to about 60° C. and dyed for 1½ hour after adding logwood. The baths exhaust well.

A logwood dyeing still frequently practised is the so-called logwood blue, which is a handsome colour, but very fugitive to light. It is produced by mordanting the goods with 8 per cent. of alum, $\frac{1}{2}$ per cent. of copper sulphate, 1 per cent. of bichromate, 4 per cent. of bitartrate, and 2 per cent. of oxalic acid, and then dyeing with logwood; the blue obtained by the use of alum alone would be too dull.

The washing fastness of the logwood dyeings is good; their fastness to light depends on the mordant used, copper and iron mordants giving fast colours, the other mordants fugitive shades. Iron black is very fast to light, but chrome black and logwood blue are fugitive, though the chrome black becomes satisfactorily fast when produced by the aid of copper mordant. On the other hand, iron black is very sensitive to acid; whilst chrome black is quite fast in this respect, dusts off to a smaller extent, and leaves the wool softer, on which account it is preferred to iron black for yarn-dyeing.

Application of the Mordant Dyes to Silk.

The mordant dyes are but rarely applied to silk; in fact, only when fastness to soap is desired. As in wool dyeing, the chrome mordants are the chief ones used, alumina mordants being only resorted to for red and orange, and iron mordants for black.

Of the mordant dyes that are suitable for silk, mention may be made of the following: Alizarine yellow GGW, anthracene yellow, mordant yellow, diamond yellow, carbazol yellow, galloflavine, cloth brown, diamond brown, alizarine orange, alizarine red (the wool marks), Kalle's cloth scarlet, anthracene red, salicine red, Domingo chrome red, galleine, alizarine Bordeaux, chrome violet, alizarine blue, anthracene blue, brilliant alizarine cyanine 3 G, celestine blue, cœruleine, diamond green, alizarine cyanine green, alizarine viridine, alizarine black, diamond black, etc. As a matter of fact, however, only a few are in general use, *viz.* alizarine red (*e.g.* the SX mark), alizarine orange, galleine, and cœruleine.

These dye-stuffs present many difficulties in dyeing silk, great care being required to get equal distribution; whilst the lustre of the silk is easily dimmed, and finally it is very difficult to obtain the peculiar "feel" so valuable in silk fabrics.

The *modus operandi* is as follows: A very rich bast-soap bath is prepared of equal parts of (weak) bast-soap solution and water, which is then neutralised with acetic acid, for pale and medium shades, or made slightly acid for dark shades. The mordanted silk is then entered cold, worked about in the cold bath for twenty minutes or so, then raised to 90° to 95° C. in about an hour, and kept at that temperature for an equal time. When soft water is used an addition of calcium acetate must be made to the bath for alizarine red.

After dyeing, the goods are rinsed, energetically soaped by boiling for a quarter of an hour with about 2 parts of soap per 1000, then rinsed again, and finally brightened with acetic or oxalic acid (20 to 25 parts of 6 B. acetic acid per 1000, luke-warm) for ten minutes.

Logwood black plays a particularly important part in silk-dyeing, and indeed, forms a special branch of this industry, quite distinct from colour dyeing.

The black dyeing of silk is one of the most difficult tasks the dyer has to perform. The art of the dyer consists in dyeing the silk and loading it to different degrees, in all imaginable shades of black, without impairing its lustre. The extent of the loading to be obtained is highly divergent, the minimum being to parity ("*al pari*"), *i.e.* the weight lost in scouring has to be made up again in loading; whilst the maximum loading attains 400 per cent. This latter degree was formerly reached in the case of souple silk for umbrellas, but is now almost entirely discontinued. The usual loading is about 50 to 60 per cent., light, souple umbrella silks being increased to the extent of 20 to 30 per cent., and heavy souples for the same purpose by as much as 190 to 200 per cent.

The requirements exacted of black silk in respect of shade, feel, and lustre are extremely varied, and the method of dyeing has to be modified in almost every case; consequently, only the main outlines of the process can be sketched here.

The silk for black dyeing is treated almost exclusively in the state of hanks. The dye used is generally a home-made preparation, a 0·1° B. decoction of logwood chips, the commercial extracts, which are prepared from more highly concentrated decoctions, containing yellow dye-stuffs, in addition to hæmatoxylin, and being therefore unsuitable for the black dyeing of silk: in fact, the handsome blue-black known in France as "*noir bleu bleu*" cannot be obtained by the use of commercial extracts.

The silk is dyed in either the souple or fully scoured state. In the latter event, the *modus operandi* is as follows: The silk is first mordanted with Rouil mordant, as described in the chapter on mordants; after which it is blued by treatment in a bath containing potassium ferrocyanide and hydrochloric acid, whereby Berlin blue is developed on the fibre. In the next place the silk is entered into a hot bath of catechu, to which is gradually added a certain quantity of tin salt, the proportion of this latter varying directly with the degree of loading required. Then follows a second bath of catechu, this time without tin, and this is succeeded by the actual dyeing with the aforesaid decoction of logwood in presence of soap. The final operation is that of brightening, which consists of treating the silk in a bath containing emulsified olive oil and acetic acid or citric acid.

This is a broad sketch of the process, which is performed in various modifications.

Occasionally, to shade the dyeing, the silk is topped with fuchsine or methylene blue in a fresh bath. To obtain a blue tinge, iron pyrolignite must be used, the following treatment being interposed between the logwood bath and the brightening process:—

A bath of iron pyrolignite;

A cold, weak logwood bath;

A cold, weak catechu bath;

A bath of soap and logwood.

To obtain a still bluer black, the treatment with iron pyrolignite must be repeated after the second logwood bath.

According to the type of black required, various modifications are introduced into the several stages of the process; thus, for example, a single mordanting and a single weak catechu bath without tin are sufficient for light souples; whereas, for a rich black ("*noir riche*") the silk must be entered five times in a strong mordant bath and two catechu baths, one of them containing tin.

For light cheap black, the blueing with potassium ferrocyanide is omitted, its place being taken by a bath of alkali blue, which, however, must be used before, and not after, the mordanting with iron. For the sake of cheapness, catechu may be replaced by chestnut extract and divi-divi for heavy souples. Finally, also the brightening process is in many instances omitted, especially when the souple is intended for moiré, in which event a softening treatment is pursued.

Some souples that are not required to be deep black are dyed, without logwood, by merely treating them with alternate baths of an iron mordant and a tannin mordant.

The particulars of dyeing two different styles of black on silk are given below.

1. *Noir Riche, with 50 to 60 per cent. of Loading.*

1. The scoured silk is mordanted five times in a 30° B. bath of Rouil mordant.

2. Entered cold in a bath of 20 per cent. potassium ferrocyanide and 25 per cent. of hydrochloric acid, the latter added in two portions.

3. The silk is entered in a bath containing 200 per cent. of catechu, at 80° C., and, when the bath has cooled down to 65° C., an addition of 15 per cent. of tin salt is given, the silk being left in the bath for five hours longer.

4. The silk is entered in a boiling-hot bath containing 100 per cent. of catechu, and is left therein overnight.

5. Dyeing with a 0·1° B. decoction of logwood and 50 per cent. of soap.

6. Dyeing with fuchsine in a bast-soap bath qualified with acetic acid, at a temperature of 40° C.

7. To the foregoing bath is added, for brightening the silk, a mixture of 5 per cent. acetic acid and 4 per cent. of olive oil in the form of an emulsion.

2. *Trame Noir Souple Persan, with 150 to 160 per cent. of Loading.*

1. Treat with 5 per cent. of hydrochloric acid at 50°. Squeeze.
2. Mordant twice in an 18° B. bath of Rouil mordant.

3. Treat in a cold bath containing 30 per cent. potassium ferrocyanide and 40 per cent. of hydrochloric acid; wash.

4. Enter in a decoction of logwood (density, 0·03° B.), at 40° C.

5. Enter in a bath of 500 per cent. of catechu, at 60° C.; heat and add 10 per cent. of tin salt when the temperature reaches 70° C., and an equal amount at 80° C. The entire operation takes a day; the goods are then washed with water at 40° C. and drained.

6. Treat for an hour in a bath of 100 per cent. of soap, at 60° C.; drain and dry.

7. Enter in the above catechu bath for one hour; wash.

8. Enter, at 50° C., in a bath containing 75 per cent. of soap and a little methylene blue.

9. Enter, at 40° C., in a bath containing 3 per cent. of gelatine and 20 per cent. of acetic acid.

10. Brighten with 4 per cent. of oil and 15 per cent. of acetic acid, at 40° C.

A cheap black dyeing for umbrella silks and linings is obtained by mordanting with basic chromium chloride, fixing with water-glass and dyeing with logwood and soap, a little fustic extract being added. The fastness of the dye to light is improved by solidification.

Application of the Mordant Dyes to Cotton.

Apart from Turkey-red and catechu dyeings, the use of mordant dyes for cotton is now very small. In this branch, and especially in the dyeing of loose cotton, there still exist various irrational methods which have been handed down by tradition, and, having been based on the dyeing of wool, are really unsuitable for cotton. These dyeings are effected by the aid of dye-wood extracts, the cotton being boiled in dissolved mordants —alum, bichromate, copper sulphate, etc.—then left exposed to the air all night, and dyed next day in a hot bath. Single-bath dyeings, darkened by after-chroming are also still not infrequently performed. Leaving these out of consideration for the present, there are really two methods in use for dyeing cotton with mordant dyes. The chief of these consists in mordanting the goods and then dyeing in a bath, which, with few exceptions, should be neutral. The goods should first be treated in the cold dye-bath for about a quarter of an hour, the temperature being then raised, in about three-quarters of an hour, to 60° to 70° C., and there maintained for three-quarters of an hour, after which the goods are washed, and, in some cases, soaped hot or warm.

By this means a series of Bordeaux, garnets, browns, and violets are obtained with alumina alone or alumina and iron as mordants, on piece-goods, the dyes used comprising alizarine, quercitron, redwood, rubine (impure fuchsine), and methyl violet, and being combined in pairs or threes not employed altogether. Thus brown shades are produced with alizarine, quercitron, and logwood, after mordanting with alumina and iron mordants, the colour being shaded, if necessary, with rubine or methyl violet. Strangely enough, the low fastness of the two latter dyes is not manifested in these combinations.

For the production of discharge effects on piece-goods and other fast dyeings chrome mordants (especially basic chromium chloride and the Hochst G.A. mordants) may be used, the dye mostly concerned being anthracene brown.

A second method consists in treating the goods with a mordant after dyeing, cutch dyeings being performed in this manner.

A third method for dyeing (mainly piece) cottons with mordant dyes is that of Erban and Specht, which, though originally designed for Turkey-red, is also applicable to the production of a whole series of lighter colours. It consists in first padding the goods with an ammoniacal solution of dye, then drying, entering in a mordanting solution, re-drying, and afterwards effecting the combination of the dye and the mordant by steaming. A similar method for chromium mordant dyeings was recommended, at an earlier date, by M. Schür.

Finally, the single-bath method can also be adopted. Suitable mixtures of dye-stuff and mordant are well known under the names of "carmine dyes" or "Boehme's dye". Methods of this kind, which are primarily intended for Turkey-red, have been recommended frequently. They consist in preparing the cotton with Turkey-red oil and then dyeing it in a bath which contains the dye-stuff, together with the mordant in a special form. The Höchst Farbwerke recommend the use of sulphites (*e.g.* a mixture of aluminium sulphate and bisulphite Ger. Pat. 123968); whilst C. Knapstein (Ger. Pat. 127698 and 146546) advises employing lactic or tartaric mordant salts.

Turkey-red Dyeing.

By the name "Turkey-red" is understood a red dyeing effected on cotton by the aid of alizarine, alumina, lime, and fatty-acid compounds. For several hundred years this colour, thanks to its beauty and fastness, has played a part comparable to that of indigo in blue dyeing. It probably originated in India, and was brought from Turkey to France, where the method of performance was published by the Government in 1765, and whence the process spread to other European countries.

The production of Turkey-red was at one time the monopoly of a few manufacturers, who kept their operations a profound secret. In more recent days, however, this industry, which previously remained without any important changes, has made rapid strides through the supercession of madder by artificial alizarine, and the introduction of modern apparatus. The principal modification of all resulted from the introduction of Turkey-red oil, which has entirely replaced the older process for dyeing piece-goods, and to a great extent in dyeing yarns as well. The superiority of the new method over the old chiefly resides in its greater brevity, the production of the red now taking only as many days as formerly weeks.

A good deal has been written with regard to the formation and composition of the colour lake here in question, and considerable research work has also been carried on in this connection. It was first discovered by Rosenstiehl that the formation of the lake from alizarine and alumina could not take place except in presence of lime. This was confirmed by Liechti and Suida, etc., it being also found that all Turkey-red dyeings contain lime.

In this dyeing process the lime can be replaced by baryta, strontia or magnesia; but, contrary to the views expressed by G. Saget, the resulting colour lakes differ, not only in shade, but also in fastness. The strontium lake comes nearest to that obtained with lime; and the poorest results are those furnished by magnesia.

The principal results of the labours of Liechti and Suida may be briefly recapitulated. If a solution of aluminium sulphate be treated with a corresponding quantity of an ammoniacal solution of alizarine, there is formed a dark red precipitate, consisting of a combination of 1 molecule of alumina with 3 molecules of alizarine.

This "normal aluminium alizarate" is readily soluble in water; whilst the basic alizarates, which contain a smaller proportion of alizarine, *e.g.* 1, 2 or 3 molecules to 2 molecules of alumina, are insoluble in water and alcohol. Alkaline solutions of the normal or basic alizarates can be mixed with Turkey-red oil or soap solution without undergoing decomposition; but, on the alkali being neutralised, red precipitates are thrown down.

Liechti and Suida also prepared the calcium compounds of alizarine. Normal calcium alizarate, $CaO . C_{14}H_6O_3$, is formed, as a blackish-violet precipitate, by the action of lime water on alizarine. The acid and basic alizarates, which are similar in appearance, pass over into the condition of the normal salt when warmed, from which it must be concluded that the normal alizarate is also formed during dyeing. Mixed with Turkey-red oil, and steamed after printing on cotton, this salt is decomposed into alizarine, calcium sulphate, and the corresponding fatty acid compound of lime. Therefore, since the steaming of the dye in presence of Turkey-red oil also occurs in the process of Turkey-red dyeing, it cannot be assumed that calcium alizarate is present as such in Turkey-red. On the other hand, one is obliged to consider lime as an essential constituent of the colour lake, the latter being therefore assumed to be an aluminium-calcium-alizarate. According to Liechti and Suida, a "normal red" has the composition $Al_2O_3 . CaO . (C_{14}H_6O_3)_3$. To produce this red upon the fibre the goods should be charged with 0·198 grm. of alumina (Al_2O_3), and be dyed with 7 grms. of alizarine (in the form of 20 per cent. paste) per metre of cloth. In comparison with the above formula all the reds met with in practice exhibit an excess—generally considerable—of alumina, which, however, neither improves the beauty nor the fastness of the colour.

The above formula for Turkey-red lake does not agree with the results of analysis. Thus, according to Rosenstiehl, the red lake contains 2 molecules of Al_2O_3 and 3 molecules of CaO to 3 molcules of alizarine, whereas, according to Sansone, the composition is 1 molecule of each of these constituents. These great differences seem to be quite explainable, however, when it is considered that this colour lake does not consist of a uniform crystalline substance. On the other hand, the true composition of such a product cannot be determined by a single analysis, any more than purple of Cassius (to take only one instance) can, even although a Berzelius should undertake the task. The only way to arrive at the exact composition of this colour lake is by the application of modern methods of investigation.

The brownish colour of Turkey-red on dyeing is probably due to the presence of calcium alizarate. This is decomposed by steaming in presence of Turkey-red oil—which accounts in part for the brightening influence of this operation. The part played by the fatty acids in Turkey-red dyeing has not yet been elucidated with certainty. It is known that fatty acids have a fixative action on alumina, as on other mordants, by forming insoluble salts therewith. Whether, however, the fatty acid alumina compound combines with the alizarine, in the formation of Turkey-red, or whether the alizarine displaces the fatty acid in order to enter into direct combination with the alumina, is a question which has not yet been decided.

Since the Turkey-red lake always contains an excess of alumina and fatty acids, it may be justifiably assumed that a portion of the fatty acids is contained, as an alumina soap, in the dye. This assumption also affords a plausible explanation of the difficulty experienced in damping yarns dyed with Turkey-red oil, and the hardness of such yarns. To some extent also the fatty acids probably remain, in the free state, mixed with the colour lake and form a mechanical protecting envelope for the colour lake, thereby increasing its fastness and lustre.

Tannic acid also plays a part in Turkey-red dyeing, since without this acid it is impossible to produce a fast Turkey-red. Its chief action is to render the dye fast to chemicking (chlorine), a matter of importance in the case of yarns that have to be woven with unbleached yarn, and then fully bleached in the piece. As in the case of the fatty acids, here also it must be assumed that the tannic acid first fixes the alumina; whether, however, it is chemically combined with the Turkey-red lake or not is unknown.

Finally, so far as the composition of the "old red" is concerned, we must assume it to correspond in the main with that of the "new red". Fatty acid compounds of the alkalis are brought upon the fibre in large quantity, and are probably oxidised into oxy-fatty acid compounds. Hence, in the subsequent mordanting with alum, there must be formed the oxy-fatty acid compounds of alumina and alkali sulphate. Moreover, old red contains a larger quantity of oxy-fatty acid compounds with alkali, as such, a circumstance explaining the greater fastness of this dye towards acids, as also the softness of the dyed yarns and the readiness with which they can be moistened.

To produce this old red, the yarn is cleansed by steeping for some time in water, followed by boiling in soda, almost without pressure, and washing. Next follows the characteristic feature of the process mordanting with oil. For this purpose the yarn is treated for about a minute with an emulsion of "tournant oil" and soda or potash, by the aid of a mechanical appliance imitative of hand-steeping, after which it is squeezed and dried. The first stage of drying consists in hanging the yarn on a series of wooden frames set up in a spacious courtyard; and from these frames the yarn is transferred to the drying chambers, where it is left for some time, e.g. overnight, exposed to a temperature of about 40 to 50° C. This temperature must not be exceeded, and for this reason provision is made in large works for the automatic ringing of an electric bell when an undue elevation of temperature occurs. When dry, the yarn must be perfectly cool before it is laid in heaps, otherwise it may be weakened as a consequence of over-heating.

This process of impregnation with oil and alkali is repeated three to five times. The more often the oil bath is used, the richer it becomes in glycerine, and therefore there must be dissociation of the oil. This probably occurs during the drying of the oil goods, whereupon the resulting fatty acids are oxidised to oxy-fatty acids, which fix themselves in an insoluble form on the fibre. The unmodified fat is finally washed out by treating the fibre with lukewarm water and a little soda, the resulting solution of soap being afterwards used as a brightening bath.

After oiling comes the sumach treatment, the yarn being steeped for several hours in a warm decoction of sumach leaves (12 to 13 per cent.); this is followed by squeezing and aluming, without any intermediate washing. The alum bath consists of a fairly strong (about 12 per cent.) solution of iron-free alum, neutralised as nearly as possible with soda. The yarn is stretched on rods and immersed in the warm liquor. The rods carry toothed wheels on their extremities, which wheels, by engaging one in another, set the rods in rotary motion, and thus enable the yarn to be reeled in the mordant liquor. When properly impregnated in this way, the yarn is left at rest in the liquor for several hours, after which it is washed, preferably with hard water (to neutralise the sulphuric acid in the bath), and is then ready for dyeing.

In Java the following method is pursued: The fabric is impregnated, four times a day, with an emulsion of castor oil, earth-nut oil and ashes, and is hung out in the sun after each soaking. This treatment is continued until the oil bath is exhausted, the fabric being then left for five days in wood-ash lye, and then washed. According to Driessen, fabrics treated in this way contain far more oil than those oiled by the other method described above. Mordanting is effected in this case by treating the fabric with certain leaves and barks, which—as Driessen was able to confirm—contain an alum salt.

Dyeing is performed in wooden vats containing alizarine (mostly with blue tinge), a little sumach, and ox blood; and, in the event of the water being soft, a little calcium acetate must be added as well. The tannic acid and yellow pigmentary matter of the sumach are absorbed first by the fibre, and help to ensure regularity of dyeing. The addition of ox blood to the bath assists in clarifying the colour, the impurities being enveloped by the coagulating albumin of the blood, and thus kept from absorption by the fibre.

The yarn, stretched on frames, is immersed in the cold bath, which is then raised to 100° C. in three-quarters of an hour, the goods being well worked the while. They are then lifted, tied together, and immersed in the bath once more, where they are boiled for a further three-quarters of an hour, in order to fix the dye completely.

To brighten the colour the goods, after dyeing, are first boiled with soda in large vessels, under a pressure of about a quarter of an atmosphere, to remove all impurities. This is followed by a similar boiling with soap; though sometimes the yarn is passed through a cold solution of the salt before boiling with soap, this treatment giving a brighter red. It is assumed that the tin is contained in the form of tin oleate in the fibre. Finally, the goods are well washed.

With the single exception of cost, this old red is superior in all its properties to the new red described below. The ratio of cost is as five to three. The fastness to acid and chlorine is greater than that of new red, and the yarn is also far softer. Yarns may also be dyed pink by the old red process.

The chief rôle played by the new red process is in the dyeing of piece-goods.[1] The operations in this new method, which owes its origin to the discovery of Turkey-red oil, are as follows: padding with the mordant, oxidising, dyeing, dunging, oiling, steaming, soaping, and washing. The first operations, which are performed in order to fix the alumina on the fibre, have already been described in the chapter on mordants, and will therefore be taken as known. The dyeing is effected in the hank, the usual adjuncts to the bath being sumach, bran, size, Turkey-red oil, and, in the case of soft water, calcium acetate. So far as the size is concerned, this adjunct is only employed as a resist, *i.e.* to protect from the dye those parts of the printed surface that are to finally appear white. The Turkey-red oil, having no particular influence on the colour, may be omitted with advantage, though still used in some works. The bran has a cleansing action on the colour lake, and the sumach plays the same favourable part here as in the old red process, both as regards the fixing of the alumina and the uniform absorption of the alizarine; however, as it stains the material yellow, it must be replaced by tannin when the production of a blue-tinged red is in question. Some also add tin preparations (*e.g.* tin hydroxide paste) to the dye-bath which brighten the red and gives it a yellower tinge. Finally, so far as the alizarine itself is concerned, the marks mostly in use are those largely consisting of anthrapurpurine. The selection of the particular mark of alizarine to produce a given shade is facilitated by making small trial dyeings with so-called "garancin strips," *i.e.* strips of cotton fabric printed with alumina and iron mordants (these are obtainable from, *inter alia*, Koechlin Frères, Mülhausen). The amount of alizarine required depends on the thickness of the cloth and the depth of red to be produced; from 8¼ to 8¾ grms. of 20 per cent. alizarine being taken per yard of 30-inch material. Bran and sumach are used in equal parts—each one-half of the quantity of alizarine employed.

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[1] According to Hummel, cottons are also dyed Turkey-red by the Steiner process, which consists in padding them in a hot oil bath, followed by quick drying at sharp heat, then padding with soda solution and drying as before, these two operations being repeated some seven times. The goods are next passed through soda and water, washed, dried, mordanted, dyed and brightened.

Greater care is needed in dyeing than with the old red process. The pieces are entered in the cold bath for half an hour, and the bath then heated very slowly to 60° C., whereupon the steam is shut off and the dyeing proceeds in the cooling bath, so that the operation takes two to two and a half hours altogether; then follow washing and drying at a moderate warmth. Overheating should be avoided, as it will affect the subsequent brightening of the colour with Turkey-red oil.

In consequence (probably) of the presence of free calcium alizarate in the colour lake, the goods have a dirty brown look at this stage. Next follows padding with Turkey-red oil solution, the stronger the better for the beauty of the colour, though this oil imparts a yellow tinge, which must be borne in mind when a bluish cast of red is desired. To give one example of quantities, 100 parts, by weight, of Turkey-red oil (90 per cent.) are taken per 1000 parts of water. For red that is to be afterwards discharged a smaller proportion of oil is taken, in order to facilitate discharging. After oiling the goods are dried and then steamed, it being noted that the red comes out brighter when the stuff is introduced in a slightly damp condition into the steaming chamber.

Steaming is performed for two to two and a half hours under a pressure of about two atmospheres, and exercises a very beneficial effect on the brightness of the colour. It is succeeded by the equally important operation of soaping, which renders the colour purer and more vivid, the process being effected at boiling-heat for one and a half to two hours, with about half a pound of Marseilles soap per sixty-yards piece of cloth. To improve the brilliance of the colour and give it a yellow cast a little sodium stannate is added to the soap bath, the same procedure being adopted when the shade comes out too full.

As an appendix to the foregoing description it must be added that the oiling process depends on the tinge—bluish or yellowish—to be developed in the red. In the former event a slight oiling is given, this taking place after dyeing; whereas in the other case a twofold oiling is applied—one before mordanting, the other after dyeing. For the first oiling, a strong solution—*e.g.* 25 parts, by weight, of Turkey-red oil per 100 of water—is used, the goods being padded with this and then dried; then mordanted as usual, fixed, dyed, and padded again, this time with a weaker solution—*e.g.* 6 per cent. of Turkey-red oil. If oil has been brought on the fibre before dyeing, this latter operation can at once be proceeded with, and at a higher temperature than that already given. In this event the reaction that, in ordinary circumstances, goes on in the steaming chamber is in part completed in the dye-bath.

Of late a very considerable improvement has been made in this new red process by abbreviating the cumbrous operation of mordanting. This improvement was based on the fact, already utilised in the old red method, that cotton containing a large proportion of oil can be mordanted with alumina by simple immersion in a solution of basic alum. The *modus operandi* is as follows: The goods are padded with a strong solution (20 per cent.) of Turkey-red oil, then dried in the hot flue, immersed for some time in a 30 per cent. solution of basic alum, squeezed, and left piled in heaps, or rolled up tightly. The manner of treating the mordanted cotton depends on the degree of basicity (by the addition of salts) of the alum solution used in mordanting. If this basicity was low, washing should be proceeded by treatment in a warm chalk bath; if high, the goods are simply washed in the cylinder machine, preferably with hard water. All the subsequent operations are performed as before. Yarns are also dyed new red in this manner.

The method of Schlieper and Baum effects the dyeing of Turkey-red in a very peculiar manner. The goods are first mordanted with sodium aluminate, and then treated several times over with chalk, in order to convert the sodium aluminate into calcium aluminate on the fibre. The dyeing is performed by passing the material through a boiling-hot solution of alizarine in lime water, in three to four minutes. After dyeing, the goods are padded with "acid soap," dried, steamed, and soaped.

Although the red obtained by this method is cheaper than that from the ordinary process, the method itself has not met with any extensive application, probably because some of the details of the manufacture are known only in the inventor's own factory.

This applies equally to the Kornfeld Turkey-red process, in which the lime necessary for the production for the red lake is added in the form of calcium saccharate, inasmuch as the process, which enables cotton yarns to be dyed in the cop, is only practised at the inventor's works at Prague.

Mention should also be made of the Erban-Specht process, which is specially adapted for the production of pink. The details of the process are given in the prospectus issued by the Höchst Farbwerke.

Colours in Competition with Turkey-Red.—Until lately alizarine was without a rival as a red dye for cotton, merely a few, quite fugitive, yarn dyeings having been performed with croceine scarlet. However, since the discovery of Congo-red and benzopurpurine, large quantities of cotton have been dyed with these in (fugitive) imitation of Turkey red.

The most dangerous competitor of the last-named dye is nitraniline red, which has largely displaced alizarine in the dyeing of piece-goods, mainly by reason of its greater cheapness, the ratio of the cost of production of the two dyeings being about 4 : 1. Moreover, nitraniline red has the advantage of dyeing the goods through better than its rival, which remains more on the surface, so that materials dyed with alizarine red are unsuitable for raising. On the other hand, nitraniline red has some very grave drawbacks, the colour being too crude and glaring, as well as less fast to light and the influence of weather than alizarine red, especially when produced without the aid of antimony. In addition its covering power is low, on which account the goods require to be well bleached beforehand, whereas Turkey-red will satisfactorily mask even a yellow cotton.

Dyeing with Catechu.

Thanks to its great fastness, this natural dye-stuff still plays a very important part in cotton-dyeing, and would be even more largely used, especially in calico-printing, if it could be discharged. According to S. Latkiewicz, however, catechu dyeings which have been produced without the aid of iron can be discharged with ferrocyanide and chlorate. It also deserves remembrance in wool-dyeing, at least in such cases where great fastness to light is in question.

Nevertheless, of late years, it has been largely displaced by the sulphur dye-stuffs, which, unlike catechu, do not harden the fibre. On account of this hardening tendency catechu is no longer used for dyeing loose cotton.

The catechu process is based partly on oxidation and partly on the formation of a lake. According to Von Cochenhausen, catechin has no tinctorial properties, these being possessed solely by catechutannic acid, which is present to some extent in catechu, and is in part formed from catechin during the dyeing process itself. For this reason, prepared catechus, obtained by heating to about 130° C. (with or without additions) are better dyes than the original catechu. This seems to coincide with the fact that a material impregnated with catechu solution comes out a much darker shade when steamed before mordanting.

Light catechu shades are produced on yarns in the following manner: The goods are dyed for a half to one hour at 60° C. with yellow or brown catechu, or a mixture of both, and an addition of about 2 per cent. of copper sulphate. They are then treated for about twenty minutes in a bath of potassium bichromate or iron pyrolignite—the former applied warm, the latter cold. Developing with chrome gives reddish-brown shades, iron-greenish tones, intermediate shades being obtained by mixing the developers.

Yellow shades are produced by adding fustic and alum to the dye-bath; for duller and more greyish tones the foregoing adjunct is replaced by logwood without alum.

Dark catechu dyeings are always produced by the aid of dye-wood extracts (logwood, fustic, redwood).

In dyeing loose cotton and yarn, the *modus operandi* is as follows: The goods are boiled for about an hour and a half in the dye-bath, containing catechu and copper sulphate, eventually also logwood or fustic extract, and then lifted and left exposed to the air. On the following day they are treated in a hot bath of potassium bichromate, and afterwards in a hot bath containing varying quantities of different dye-wood extracts, according to the shade required. This final dye-bath occasionally receives an addition of alum, or also tin salt for reddish tones.

Piece-goods are first padded with a weak acetic acid solution of catechu, and dried, then passed through a hot solution of potassium bichromate, partially neutralised with soda, rolled up, and left alone for some time. In the case of dark shades, the pieces are passed a second time through the chrome bath and left rolled up for several hours. Yellower tones are obtained by adding alum to the chrome bath; still yellower shades by adding alum and fustic extract; whilst, for very dark shades, an addition of logwood extract is given.

Catechu dyeings are frequently shaded by the aid of basic dyes, applied in a fresh bath in association with alum.

Black-Dyeing Cotton with Logwood.

The employment of logwood in the black-dyeing of cotton has suffered considerably from the competition of aniline black and various substantive dyes. Its chief use nowadays is for greys on linings.

The first black on cotton was produced with sumach and iron mordants, the colour, however, being only a dark grey. At present there are two chief methods of dyeing cotton black with logwood. The first of these, which is mainly employed for loose cotton and yarn, consists in producing a colour lake from logwood, tannic acid, and salts of iron and copper, in various ways.

The most rational of these is the following: The cotton is first left overnight immersed in a decoction of 40 per cent. of sumach; it is then squeezed and treated for half an hour in a cold solution of iron pyrolignite (of about 3° B. density), followed by passing it through very dilute lime-water, and thoroughly washing. By this means iron tannate is produced on the fibre; the lime treatment serves to neutralise the acid. The iron pyrolignite may be replaced by "iron nitrate" or ferrous sulphate, a little levigated chalk being added to the bath in the latter case. A handsomer black is obtained by the use of alumina mordants—a little aluminium pyrolignite, for example, being added to the iron bath.

The cotton thus prepared is next dyed with logwood, sometimes in presence of a little fustic, by entering in the cold bath, which is then slowly raised to boiling. To increase the fastness of the black, the stuff may afterwards be treated in a bath of bichromate (½ part per 1000, at 60° C.) or iron nitrate. Sometimes the shade is darkened in the dye-bath itself by an addition of copper sulphate.

Finally, the cotton is soaped, a treatment that makes the tone of the black more agreeable.

The numerous variations of this method have been described by Ed. Weiler (Lehne's *Färber Zeitung*, 1889-90, p. 137).

The following method is generally employed for the production of mourning goods in piece dyeing: The stuff is padded with a mordant solution consisting of 3 parts of iron pyrolignite (6° B.) and 7 parts of aluminium pyrolignite (7° B.), then fixed and dyed in a bath containing, in addition to the necessary quantity of logwood and a little quercitron, 2½ oz. of borax, 1¼ lb. of sumach, and 5½ to 6½ lb. of cow dung, per 22 gals. of bath liquor. For the first quarter of an hour the bath is cold, after which time it is heated so as to bring the temperature up to 80° to 90° C. in about an hour. After dyeing, the goods are washed, treated with bran, and washed again. The bran bath is prepared by boiling bran—packed in close bags—in water, in the proportion of one part, by weight, to 100 parts of water, the cotton being then treated in this hot liquor for twenty minutes. At present this black is dyed with aniline black by the Prudhomme process.

5. Application of the Sulphur Dyes.

The sulphur dyes are used in strongly alkaline baths and are therefore adapted only for cotton. For this purpose, however, they have very largely displaced the substantive dyes of late years, because their dyeings are very fast to washing, and for the most part also faster to light than the substantive dyes.

Both the sulphur dyes and the sodium sulphide used in the dyeing process should be stored in a dry, cool room and be well covered up. They must not be allowed to come in contact with copper or brass, though iron and lead have no injurious effect.

Dissolving is effected in wooden vessels, the dye-stuff being first mixed with its own weight of sodium sulphide (or 2 to 3 times that weight in the case of the "extra" marks of dyes) and then treated with hot water until a clear solution is obtained.

As a rule, sodium sulphide, carbonate of soda and salt (Glauber salt) are the only additions to the bath, and in fact most of these dyes can be used without the first-named if a strongly alkaline bath be used. In exceptional cases caustic soda is added to facilitate solution; whilst Turkey-red oil assists the penetration of the dye, or dextrin may be employed for black.

The bath should be fairly strong; about 1 : 10 for loose cotton and 1 : 15 for yarns; though, of course, weaker baths are used for light shades.

The quantity of dye-stuff used amounts to 10 to 20 per cent., or more, for dark shades. The amount of sodium sulphide added is usually constant, but in any case enough must be taken to give a clear liquor.

Dyes that do not equalise well require an extra quantity of sodium sulphide to check uneven dyeing, and the same applies to the dyeing of light shades. From 50 to 100 per cent. of common salt is added to ensure more complete extraction of the dye—but for light shades, only ⅓ to ⅕ the above quantity is needed.

In preparing the dye-bath, the requisite amount of water is boiled, with addition of 5 to 10 per cent. of carbonate of soda, and then the sodium sulphide, dye-stuff solution and other additions are introduced. The baths being strongly alkaline, care should be taken not to immerse the hands in the liquor unless protected by rubber gloves.

Dyeing is conducted as follows: The goods are entered into the boiling bath, and are left in for about an hour—more for dark shades and less for light—while the bath cools slowly. At first, the goods should be turned about every five to ten minutes, and at longer intervals afterwards. It is immaterial whether cottons are exposed to the air or not, for any stains that might be formed by oxidation would disappear during the further course of the operation. Nevertheless, it is desirable to prevent the formation of stained patches, which can be done in the case of yarns by dyeing on bent gas piping, and in the case of piece-goods by using a submerged jigger. In view of the tendency of most sulphur dyes to stain in patches, it is most important to ensure uniform squeezing immediately after dyeing, a pair of squeezing rollers being, consequently, mounted on the dye-vat. Most sulphur dyes also require washing directly after squeezing; and since the rinsings become enriched with sodium sulphide and dye-stuff, they can, after repeated use, be employed for dissolving the latter. Spotty dyeings can be treated in the lukewarm rinsing liquor, a little sulphide being added if required, and, after a short time, the spots will mostly disappear. In this way, too, unsuccessful dyeings may be put right.

The foregoing is the ordinary way of using the sulphur dyes. Some of them can also be dyed in the cold, *e.g.* katigene-indigo B extra, and katigene dark blue R extra; in some cases, such as immedial pure blue, a dyeing temperature of 20° to 30° C. (68° to 86° F.) is preferable to boiling-heat. Certain of these dyes (*e.g.* immedial blues C and CR) require to be oxidised in order to exert their tinctorial properties fully. In such cases the cottons are not rinsed after squeezing, but are either exposed to the air or else placed in a vat (lined with packing cloth) and treated for about three-quarters of an hour with steam, charged with air by attaching an air injector to the steam pipe. This treatment is followed by washing.

Spent baths can be used over again, the amount of additions they contain being roughly estimated by a hydrometer. Baths for black have a density of about 6° to 7° B.; other dark colours about 3° B.

Iron baths should be rinsed out with a solution of carbonate of soda, to prevent rusting.

Tinned centrifuges are best for draining the dyed goods.

After-treatment.—Whenever possible, dyeings made with sulphur dyes should not be shaded, because the basic dye-stuffs draw too rapidly and therefore give patchy results, though this can be avoided by using small quantities of such dye-stuffs in the soap-bath. The substantive dyes, which naturally come to mind in this connection, cannot, in this case, be used for shading in the dye-bath itself, since most of them are decomposed by sodium sulphide. The most resistant in this respect are the dye-stuffs of the chloramine yellow group. Topping with substantive dyes in a fresh bath is inadvisable for several reasons. The best dyes for shading are such mordant dyes as equalise readily; but these can only be used in such dyeings as have been subsequently treated with mordanting salts.

For economic reasons, the after-treatment of sulphur dyeings with metallic salts is rarely practised. A few of these dyeings —greens, for example—are even changed unfavourably thereby, becoming bluer and duller. For others, however, such as melanogen blue and most of the sulphur dyes, such after-treatment is indispensable for obtainings that will stand storing and washing. Various metallic salts are used for this purpose; for example, a mixture of 1½ to 2 per cent. each of bichromate of potash and copper sulphate,[1] to which is added a little acetic acid. Either of these salts may also be used alone. The bath liquor should have a temperature of 50° to 90° C. (122° to 194° F.); but it must be borne in mind that many dyeings are spoiled by the bath being too hot. In special cases, alum, chrome alum, and salts of zinc, cadmium, etc., can also be used for this after-treatment; but as already stated, after-treatment should always be avoided wherever it is possible to do so.

Dyed yarns may be brightened and softened by treatment in a boiling bath of starch and lard, or oil and soap, with addition of a little sodium acetate, and then unwound and dried.

Chloring destroys most dyeings with sulphur dyes.

Mercerised Cotton must be carefully dyed, because of its unusual high affinity for dye-stuffs and consequent proneness to irregular dyeing. It is therefore dyed in very dilute baths, with a larger proportion of sodium sulphide and less salt than ordinarily.

Silk also dyes well with sulphur dyes, and the dyeings will stand washing. Sodium sulphide, glucose, Turkey-red oil, and Glauber salt are used in the preparation of the bath.

6. Application of the Vat Dyes.

The vat dyes are insoluble in water, and therefore cannot be used directly for dyeing. On the other hand, their leuco-compounds are soluble, have a very decided affinity for the fibre, and are also gifted with the property of being readily reconverted into the dyes themselves under the influence of weak oxidising agents. Consequently, in order to dye with these dye-stuffs, all that is necessary is to impregnate the fibre with the reduced dye in solution, and then expose it to the air. The fibre absorbs the leuco-compound of the dye-stuff, which is then reconverted by the atmospheric oxygen into the corresponding insoluble dye, the latter being precipitated firmly in and upon the fibre.

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[1] The goods must first be well rinsed in order to prevent precipitation of the copper by sodium sulphide.

This method has been practised from time immemorial with indigo, and plays a highly important part, inasmuch as indigo has been, and still is, the chief vat dye-stuff known.

Until recently, indophenol blue was the only member of this group, except indigo; but at present a whole series of valuable new dye-stuffs of this class are available, from the anthraquinone group, such as indanthrene, flavanthrene, etc., as well as thio-indigo red. The following description is confined to the method of dyeing with indigo, the instructions for the others being supplied by the makers in their prospectuses, etc.:—

"Vat dyeing," or "blue dyeing," is the term usually applied to dyeing with indigo, since, with the exception of the comparatively unimportant indigophenol, no other dye is applied in this manner, nor can indigo itself be fixed on the fibre in any other way.

The term "vat" applies to the vessel employed for dissolving the indigo, and also to the solution itself. This latter is prepared by the aid of various reducing agents, which, however, can only be used in presence of an alkali, the resulting indigo white being insoluble except in alkalis.

The vats may be divided into warm and cold, or fermenting and non-fermenting, vats. To the fermenting vats belong the woad, soda, potash, and urine vats; they are warm vats and are employed exclusively for wool.[1] The non-fermenting vats comprise the zinc or preparing vat, the vitriol vat, the hydrosulphite vat, and the indigo-indigophenol vat. The first two of these are cold vats, and are therefore used solely for vegetable fibres; the others are warm vats, and can be applied to the dyeing of both vegetable and animal fibres.

Whichever vat be employed, the first task is essentially the careful comminution of the indigo, since it is only when this substance is in a fine state of division that it can be brought into solution by reducing agents. For this purpose the indigo is mixed into paste with water and alkali, and ground for some considerable time in an indigo mill, of which there are numerous types. Of course, when "pure indigo," "indigo MLB" (in paste) or "indigo MLB, vat" (a highly reducing mark) are used, this grinding is superfluous.

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[1] In the Orient these vats are still used for dyeing cotton and wool in the yarn, but not elsewhere.

The most important of the fermentation vats is the woad or "bastard" vat, so called because of the addition of soda now practised. It plays a principal part in the dyeing of wool, and is used solely for this purpose, the warm vats as a whole being ill adapted for dyeing vegetable fibres, whilst the application of indigo to silk dyeing has now been abandoned.

The fermenting materials used in the preparation of the woad vat are woad, madder, bran, and syrup, the woad playing the chief part in the mixture. The addition of madder is in so far favourable that, apart from its fermentative action, this substance takes part in the dyeing process by virtue of its tinctorial character, a valuable consideration when dark shades are in question. The Bran acts as an instigator of fermentation, and, in addition, imparts to the bath liquor a certain degree of viscidity favourable to the suspension of the indigo that is to be dissolved therein. However, since the presence of a large quantity of bran would tend to choke the vat, a portion of this substance is replaced by syrup.

The alkaline adjuncts to this vat are lime and soda. They serve to neutralise the acidity engendered by the fermentation, and to maintain the liquor in the state of alkalinity essential for bringing the indigo white into solution. In addition, they retard fermentation, and therefore afford a means of regulating the progress of this operation.

The woad vats are usually round in shape, measuring about eighty inches across and eight feet in depth, and are set about two-thirds in the ground; for yarn-dyeing they are mostly square.

The vats are started by powdering the woad, mixing it into a paste with boiling water and leaving to stand for some time, after which it is introduced into the vat, filled with water, the madder, bran, lime, soda, and ground indigo being then added. The proportions employed are—woad, 220 to 230 lb.; indigo, 11 lb.; madder, 33 lb.; bran, 33 lb.; lime, 4½ lb.; soda, 22 lb.

The vat is now heated to 100° C., stirred up well, and covered up, after the fire has been drawn, in order to keep warm as long as possible—an essential condition for the inception of fermentation. After standing twenty-four hours the vat is uncovered to see whether fermentation has begun, which will be the case if the liquor "works," *i.e.* throws up a number of small bubbles; whilst the initially blue colour of the liquid has now become a yellowish-green, a blue scum floats on the surface, and the smell has changed. Should these indications be absent the vat is covered up again and left to itself for some time longer before being reinspected. As a rule, the woad vat will have begun to ferment in two to three days, though the actual time may vary according to the time of year.

When fermentation has commenced, the vat is limed by adding finely sifted slaked lime at intervals of two to three hours, stirring the contents up well after each addition. By this means the acidity produced during the fermentation is neutralised, and the fermentation restrained at the same stage for some time, in order to bring the whole of the indigo into solution. The newly started vat cannot be used for dyeing immediately, because at this stage the fermentation and the solution of the indigo are only just begun; in fact, the vat is not fit for use until it has been limed several times and a large proportion of the indigo has been brought into solution. The vat in this stage exhibits the following characteristic indications: The vat liquor is olive-green in colour, and carries on its surface a layer of copper-blue scum the "bloom," ½ to 1 inch deep; the smell is peculiar and faintly ammoniacal; and, where the separated scum has left the surface visible, a number of blue "veins" appear. When the vat has arrived at this stage, it must be used at once for dyeing, and not left any longer, otherwise the fermentation will proceed at the expense of the indigo. The woad vat can be kept in use for several months in succession, provided it be maintained in good condition in the following manner, the process, however, being one of the most difficult tasks the dyer has to perform: After dyeing a whole day, the vat is reinforced in the evening by the addition of a certain quantity of madder, syrup, and lime, then heated, well stirred up, and left covered up all night for use the following day. In order to replace the loss of indigo sustained in dyeing, an addition of this dye-stuff must also be made at intervals, every day or second day.

The two extremes to be avoided are excessive fermentation owing to an insufficiency of lime, and a cessation of fermentation through an excess of that adjunct. The former condition, known as mildness, because of the sweetish odour evolved, can be remedied by adding lime at intervals until the smell and appearance resume their normal condition. If, on the other hand, the vat contain too much lime, it is considered to be sharp, and will smell strongly of ammonia, in which event the excess of lime must be neutralised by a gradual addition of acid, the fermentation being restarted by the aid of bran. Unless excessive fermentation be checked in time by adding lime, the colour will be wasted; and the final condition of a sharp vat is blackening. In either event, it is often impossible to remedy the defect, and the liquor has to be run to waste. This can, however, be avoided by careful supervision; the dyer must be able at any time to tell, from the appearance, smell, and behaviour during dyeing, whether the vat needs an addition of lime or a ferment.

Vat-dyeing is performed at a medium temperature (about 50° C.), and in this case, more than any other method of dyeing, great care is necessary to see that the goods are thoroughly damped beforehand. The scum must be removed before entering the goods. Loose wool is invariably dyed in circular vats, the wool being enclosed in a net, completely immersed in the vat liquor, and worked about therein by means of sticks. After about an hour it is lifted and well squeezed to express the excess of liquor. At this stage the colour is green and has to be developed into blue by oxidation, for which purpose the wool is thrown in a heap on the floor and shovelled over so as to expose all parts to the air. If the vat is in good condition the lifted wool will have a yellowish-green shade, which afterwards turns dark green before arriving at the blue stage, the latter being attained gradually. If the change occurs too quickly, the vat is too sharp; and converse behaviour indicates excessive mildness, the condition of the bath being thus determinable by dyeing a small sample and observing its behaviour after lifting. Occasionally such parts of the wool as have not come in contact with the air remain quite white. The development of the blue will be complete in about a quarter of an hour, whereupon the wool can be re-entered in the vat if a darker shade is required.

To produce a bright light blue, a fairly fresh vat is essential, and this must contain less lime, and consequently more soda, than usual. However, the vat should not be quite fresh, since the first parcel dyed in the vat is always dull and muddy in colour, in consequence of the dun-coloured pigments of the madder and the woad. Finally, this vat must be rather weak in indigo.

To match a dark blue exactly to pattern, the goods must first be blued in a strong vat until the desired shade is nearly attained, and then finished in a weak vat.

Yarns are suspended on smooth sticks, then immersed in the vat liquor, and kept well worked about therein, after which they are lifted, squeezed, and left to blue.

For piece dyeing, the vat is fitted with an attachment which enables the goods to be kept in motion all the time and below the surface of the liquor. At the end of one to two hours, according to the strength of the vat and the depth of colour to be produced, the pieces are unwound and the superfluous liquor squeezed out between rollers. To develop the colour the pieces are alternately folded and opened out, and are finally washed. This must be done very carefully in indigo dyeing, fuller's-earth being used with piece-goods. Vatted pieces must not be left for any length of time in a warm place before washing, or they will be liable to turn mouldy.

The other fermentation vats are managed and applied in the same way as the woad vat. The soda vat alone is of any practical importance, and is used for dyeing bright shades of blue. Its operation necessitates greater skill than is required for the woad vat process, from which it chiefly differs in the fact that carbonate of soda is practically always used. The usual adjuncts are bran, madder and syrup. If such bright blue dyeings are only occasionally required, the usual practice is to continue the woad vat in use as a soda vat instead of preparing the latter specially. Of late years, bright coppery blues are also obtained with artificial indigo.

Frequently, in order to save indigo, vatted goods are topped with logwood, for which purpose they are first mordanted with alum, copper sulphate, potassium bitartrate, and oxalic acid, and then dyed with logwood. In other cases, however, they are mordanted in the same manner as for logwood blue (*q.v.*), which is a decided irrational process, the greater part of the indigo on the fibre being destroyed by boiling in the bichromate bath. These dyeings are known as "semi-fast blue," being less fast to light than vat blue.

Occasionally the topping with logwood is only intended to secure better equalisation of the dye, uniformity being difficult to obtain on piece-goods in vat dyeing.

To produce a semi-fast blue with a blackish appearance—which though less brilliant than, is quite as fast to light as, true vat blue, and is also fast to wear—the goods are first blued in the vat, then boiled with santal, and afterwards vatted anew.

It may also be mentioned that some dyers in producing dark blues dye the goods first with azofuchsine, because this dye-stuff cannot be detected by the indigo test (reaction with concentrated sulphuric acid).

The Hydrosulphite Vat.—This vat is dealt with in connection with the fermentation vats, inasmuch as it also is used warm and is chiefly employed in wool-dyeing.

It presents numerous advantages over the woad vat, including: easy manipulation, which renders careful supervision superfluous; dyeing can be commenced as soon as the vat is prepared, and the vat can be left idle at any time. For medium blues, at any rate, the vat is more productive than the woad vat, and the indigo is more efficiently utilized. The amount of sediment is but small, and even the lighter ("pearl") shades of blue can be dyed with perfect uniformity without leaving any "white tips" in the wool. For such cases the hydrosulphite vat is really indispensable. It is mainly used for pale and medium blues on woollen yarns, but it also gives better penetration in the case of piece dyeing as well. For loose wool, on the other hand, the woad vat is still mostly used.

At present, artificial indigo alone is used for dyeing by the hydrosulphite vat process. Of the three forms—indigo powder, paste and reduced indigo—supplied by the manufacturers, the paste (20 per cent.) finds the largest employment. From this a stock vat is prepared by warming it to about 50° C. with sodium hydrosulphite and caustic soda, or lime, though vats prepared with the last-named substance have the disadvantage of depositing a sediment. The vat can also be prepared in the manner already described in the chapter on Bleaching Agents, but this method is profitable only in large works.

Owing to their strongly alkaline character, the caustic soda hydrosulphite vats require care when used for wool, and the workers must wear rubber gloves. Ammonia is the most suitable alkali; and this is added to the dye vat, the alkali of the stock vat being neutralised with ammonium chloride. In order, however, to keep the indigo white in solution in such faintly alkaline baths, a solution of glue must be added.

In preparing the vat, it is first charged with warm water containing hydrosulphite, a quantity of the stock vat sufficient for the desired blue being then added and stirred up. Dyeing may be commenced at once. When ammonia is the alkali selected for the dyeing process it is added to the water first, being followed by the dissolved glue and finally by the hydrosulphite and stock vat—or a caustic soda vat is treated with glue solution and the corresponding quantity of sal ammoniac. The higher the alkalinity of a vat, the longer does the dyeing process require, and therefore only very little ammonia—just sufficient for a test sample of the vat liquor to give a fugitive slight red tinge with phenolphthalein—is used for dyeing dark blue shades. For lighter shades the amount of ammonia is correspondingly increased; and for these shades the proportion of hydrosulphite should also be higher in order to ensure uniform distribution.

The advantage of dyeing in an ammonia vat is that the wool retains its softness unimpaired.

Light shades are dyed by a single dip, darker shades by several dips, at a temperature of about 50° C. For these latter shades it is advisable not to dye too deeply at first. It is of interest to note that more indigo is absorbed by the fibre in the second dip than in the first.

The dyed wool is squeezed on issuing from the vat, the expressed liquor running back down a sloping board. The usual after-treatment is then given.

For very light shades on worsted yarns it is advisable to proceed in a different manner.

The principal consideration here is perfect equalisation, and this depends on two circumstances—(1) the well-damped yarn must be carefully separated into individual hanks, each of which is then suspended from a separate very smooth hazel rod; (2) the conversion of the green dyeing into blue must be performed in the most careful manner possible, as described in detail below. If these conditions are not properly fulfilled, the colours will be uneven and mixed.

The rods laden with yarn are set side by side in a wooden frame, without touching one another, the whole being then slowly dipped into the vat. Here they are turned by hand at intervals, and remain until it is quite certain that the absorption of dye has ceased. This is necessary, because the hanks cannot be all taken out at the same time, but must be lifted in succession; and since it is essential that the whole parcel should be uniform in depth of colour, no opportunity can be allowed for any of the hanks to absorb more dye than the rest.

The absorption will be complete in about half an hour, whereupon the hanks are lifted from the vat one after another, rapidly squeezed, and then rinsed in cold water in the following manner: Three or four tanks, about 10 feet long by 40 inches wide, are placed in a row close by the vat, and through these the yarn is passed in succession, being opened by a pair of workers in the first tank, worked round, taken over, and treated in a similar way by a second pair of workers, and thereby advanced a stage, the operations being repeated until the end of the last tank in the row is reached, whereupon the yarn is squeezed and drained in the hydro-extractor.

The object of this treatment is to remove the superfluous vat liquor from the yarn as quickly as possible, and enable the blueing process to proceed gradually. The water in the said tanks must be renewed at intervals during the progress of the work. This applies particularly to the first tank, since this receives the largest quantity of vat liquor. The changing can be effected by making the feed and discharge continuous.

The colour of the freshly lifted yarn is yellow, changing to green in the first rinsing tank, and then gradually turning blue, the change not being quite complete till the yarn has passed through the hydro-extractor.

In this manner the palest blue shades can be obtained in perfect uniformity and clearness.

By adding bisulphite to a hydrosulphite vat of suitable strength, until an acid reaction occurs, a dark blue can be obtained in one dyeing. If such vat is then to be used again for dyeing, its alkalinity must first be restored by the addition of ammonia. This process is best adapted for dyeing worsteds by machine, the multiple-dye method being preferable for the ordinary dyer when dark shades are required.

At intervals—about twice aday—the hydrosulphite vat requires a fresh addition of hydrosulphite, and a little fresh stock vat liquor about once a day. The presence of an insufficiency or excess of reducing agent can be gauged by the colour of the liquor, and the degree of alkalinity by the aid of an indicator.

VAT DYEING ON COTTON.

What the woad vat is for wool, the zinc vat is for cotton and linen. It has for the most part displaced the old vitriol vat, and is now almost the only vat used for cotton-dyeing. Its action is based on the property possessed by zinc dust of readily decomposing water in presence of an alkali, and combining with the liberated oxygen, whilst the hydrogen reduces the indigo blue to indigo white, which is immediately dissolved by the alkali.

Lime is the alkali generally used here.

A stock vat is first set by mixing together 10 parts of ground indigo, 7 parts of zinc dust, and 20 parts of lime, to form a pulp with water, and leaving the whole to "ferment" in a tub. In about twenty-four hours the process of reduction will be complete, whereupon a portion of the contents of the stock vat is transferred to the dye vat, stirred up in the cold water with which the latter is filled, and left at rest until the liquor has clarified, by which time the vat will be fit for use. The zinc vat varies in size and shape, but in the usual round form the ratio between depth and diameter is about 2½ : 1.

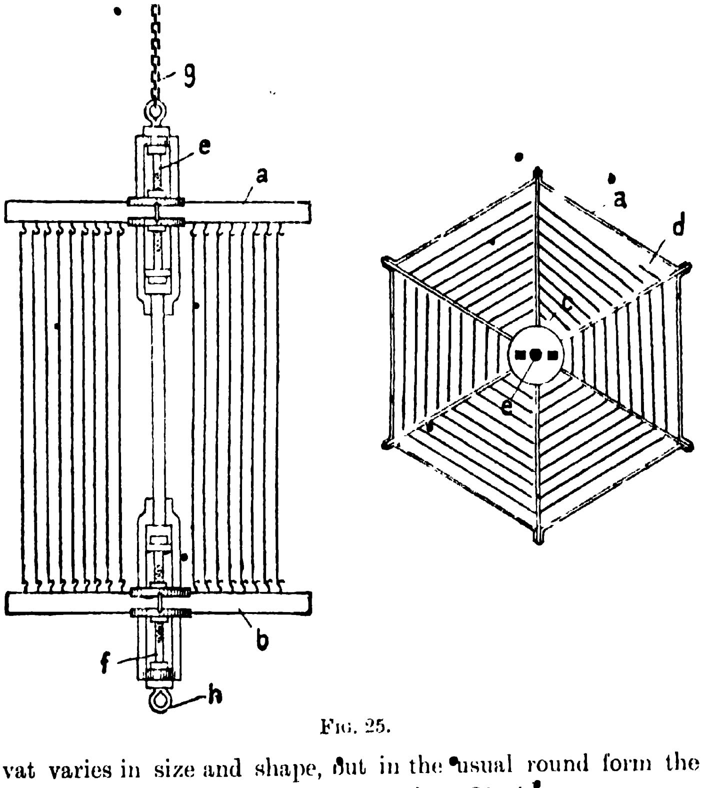

FIG. 25.

The appearance of the zinc vat differs little from that of the woad vat, whilst the management is much easier, all that is necessary being an occasional replenishing from the stock vat or an addition of zinc dust or lime. If the vat liquor be green, too much indigo is present; if yellow, too little. When there is a deficiency of lime the vat becomes turbid through the evolution of hydrogen. After each addition to the vat the liquor must be stirred up and then left to settle before use.

Cotton may be dyed in this vat in all stages of manufacture; most frequently in piece form, less often as yarn. The piece of cloth to be dyed is wound on the frame shown in Fig. 25 in such a manner as to preclude contact between any two adjacent layers; and, after the scum has been removed from the vat, the frame is immersed in the liquor and kept therein for five to ten minutes. The frame is then lifted and kept in the air for an equal time, in order to develop the colour. If the goods be dyed in several dips, the frame must be reversed after each, or else the lower part of the cloth will come out darker than the rest. After dyeing follows "souring," which consists in entering the cloth, full width, in sulphuric acid of about 2° B. density, to remove adherent calcium carbonate and consequently brighten the colour. The operation is completed by washing. The indigo dissolved in the processes of souring and washing must be recovered.

If the blue be desired to have a coppery appearance, the goods must be dried by heat. The brilliancy of the colour may be improved by methylene blue and methyl violet, these being, however, applied in the dressing, and not in the dyeing process.

Frequently, and especially in yarn-dyeing, the operation of vatting is preceded by a bottoming with some other dye. This is primarily intended to economise indigo, but the goods are also dyed through better, and sometimes also the tendency of the vat blue to rub off is diminished by this means. The dyes used for this purpose are Columbia-black R, diamine black, Chicago-blue, benzo blue-black, etc. In small dyeworks topping with logwood is often practised, the dyed cotton being treated in a bath of logwood, alum, and copper sulphate, or else first entered in a solution of iron pyrolignite and then dyed with logwood and alum. Dark blues, to stand calendering, should be topped with sumach and iron.

Finally, it may be mentioned, that the dyed yarns are often treated in a hot chalk bath, which diminishes the tendency of the colour to rub off.

The most important improvement in piece dyeing was the introduction of the continuous vat, a process wherein the alternate dipping and lifting of the goods is effected in a continuous manner by leading the cloth upwards and downwards over a series of rollers, partly in and partly out of the vat. The roulette vat is a kind of double vat, the dyeing process corresponding to a double passage through the continuous vat.

The continuous vat process is superior to the older method in every respect; the blue is handsomer and better fixed; less indigo is lost in the washing, and, owing to the pressure of the squeezing rollers, the goods are dyed through better and a better green is obtained; moreover, there are fewer light patches, and even dead cotton is dyed. For discharge effects this vat alone is employed, on account of the necessity for having a handsomer blue than is required when the goods are of one colour throughout. A variety of this process is used in England for yarns.

The vitriol vat is set with indigo, ferrous sulphate, and lime;[1] the management and application are the same as for the zinc vat.

It was largely used at one time, especially for dyeing yarns, but of late years has been given up, almost entirely, on account of the considerable sediment formed, which is a source of trouble in dyeing and also of loss of indigo. The only advantage with which this vat can be credited is that it dyes more slowly than the prepared vats and that the medium and dark blues are of a redder tinge.

The indigo-indigophenol vat is set in a similar manner to the hydrosulphite vat. Its advantage consists in replacing a portion of the indigo by the cheaper indigophenol. It is, however, not very easy to manage, owing to the difficulty in regulating the addition of hydrosulphite, and has not attained any practical importance.

Dyes Competing with Indigo.—Attempts have been made to supersede indigo, for wool-dyeing, by a number of blue mordant dyes, such as alizarine blue, anthracene blue, alizarine cyanine, brilliant alizarine cyanine, etc., with some degree of success;* and at the present time a number of dyeings that were formerly performed with indigo exclusively are carried out with these substitutes.

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[1] The approximate proportions are: 25 parts by weight of ferrous sulphate and 30 parts of lime per 10 parts of indigo.

The superiority of indigo over these rivals consists in the handsomer and fuller appearance, conjoined with the unsurpassed fastness of the colours to light. True, indigo fades a little under the influence of light; nevertheless, the blue, even in the lightest shades, always retains its handsome, bright tone, which is not the case with the other dyes mentioned. In fact, the latter can only replace indigo for dark shades, leaving it unrivalled for light blues, especially since the introduction of the hydrosulphite vat.

For cotton-dyeing a number of basic dyes, such as indoine, naphtindone, diazine blue, new blue, indophene blue, indol blue, indamine blue, indophenine, meta- and paraphenylene blue, etc., have been employed to imitate indigo. However, when subjected to test, the resulting dyeings are far inferior in fastness to indigo, and the superiority of the latter becomes still more apparent. Under the action of acids, bleaching powder, washing, and light, indigo dyeings suffer merely quantitative alteration, the brilliant blue colour remaining unchanged. The rival dyes, on the other hand, mostly become discoloured, often reddish-grey, and, in the dark shades, mostly rub off quite as much as vat dyeings.

Owing to their tendency to redden (through the formation of safranine) in presence of reducing agents like syrup, dextrin, etc., the indoine blues, which are the most suitable for this purpose, have been practically abandoned as substitutes for indigo.

The dianisidine blues cannot be used, by reason of their non-resistance to acids and the difficulty of getting equal distribution. On the other hand, the application of indigo to dyeing cottons has been considerably lessened by the use of substantive dyes developed on the fibre or treated with copper, *e.g.* diamine pure blue (coppered), diaminogen blue, diamine azo blue, diazo-indigo (developed), etc., and especially by the fast blue sulphur dye-stuffs.

7. Application of the Developing Dyes

The developing dyes are not purchasable in the finished condition, but are produced on the fibre. They are applied solely to cotton, and are distinguished by their fastness. They are divided into three groups—(1) the ice colours; (2) colours developed on the fibre; (3) colours produced by oxidation on the fibre; (4) mineral dyeings.

Before proceeding to a special description, the following observations should be made: The first stage in the production of these dyeings on piece-goods consists in bringing the dissolved potential dye-stuff upon the fibre by padding, squeezing, and drying. In performing these operations it must always be borne in mind that the amount of the substance thus brought on the fibre depends not only on the strength of the solution, but also on the pressure of the squeezing rollers employed, which must therefore receive particular attention.

The name "ice colours" is applied to a series of insoluble azo dyes, which are produced on the fibre, from their components, by the aid of ice as a cooling agent. The first processes of this kind were those described in the patents of Read, Holliday & Sons, of Huddersfield (1880), and Fr. Grassler. Great difficulties had, however, to be overcome in applying the method on a large scale, and it was not until the end of the eighties that J. J. Weber, of Winterthur, succeeded in producing a red from amidoazobenzol and β-naphthol on the fibre, on a manufacturing scale. Credit is also due to the Hochst Farbwerke in particular, in connection with the further extension of these dyes, which, thanks to their cheapness and beauty, now play a very important part.

The method actually practised is briefly as follows: The well-bleached cotton pieces are padded with a solution of β-naphthol in caustic soda, then dried, and afterwards passed through a solution of a diazotised amine, cooled by means of ice. The chief dyeings are—

Scarlet with p-nitraniline;
Bordeaux ,, a-naphthylamine;
Brown ,, benzidine sulphate, with or without addition of a-naphthylamine.

In addition, for reds, there are azophore red, nitrosamine red, phenetidine red, and, for a yellowish Turkey-red, β-naphthylamine; for blue, dianisidine blue, azophore blue; and for fast (azo) garnet, amidoazotoluol—to be considered as amines.

For blacks, a whole series of combinations has been proposed, and to some extent adopted in practice, though none of them has really succeeded in solving this difficult problem. The following are the most suitable compounds: the Höchst azo black base (a mixture of benzidine and dianisidine), azophore black (*p*-diamidodimethyl carbazole), and Cassella's azotol C (amidochrysoidine) which give a black with β-naphthol; the combinations: nitraniline and Cassella's naphthol BD (1.6 and 1.7 amidonaphthol); nitraniline and Badische nigrophore (obtained by coupling diazotised 1, 2, 4 dichloraniline with 1.8 amidonaphthol-5-sulphonic acid in acid solution); benzidine and Bayer's developer ES (2.3 dioxynaphthalene-6-sulphonic acid).

The different manufacturers of dye-stuffs are busily endeavouring to increase the number of these dyes and to improve those already known. This applies particularly to nitraniline red and dianisidine blue, the endeavour being to produce the former in a more bluish tinge, similar to Turkey-red, whilst with dianisidine blue the endeavour is to improve its worst quality—the lack of fastness to perspiration.

The β-naphthol is dissolved in pure caustic soda, care being taken to avoid any excess, because of the resulting increased tendency of the β-naphthol to turn brown, by oxidation, on exposure to the air. This defect may be ameliorated by the addition of solutions of an antimony salt in glycerine (Lauber and Caberti's patent), one of which is sold under the name "Naphthol LC". Sulphites, too, improve the stability of the naphthol solution, though to a smaller extent. Owing to their tendency to absorb carbon dioxide from the air and then deposit the β-naphthol, these solutions should be kept in closed vessels.

For reds, the naphthol solution receives an addition of a fatty preparation, *e.g.*, Höchst para-soap PN (an acid, castor-oil ammonia soap) which gives a handsomer colour with a more bluish tinge. For such shades the ordinary β-naphthol is replaced by naphthol R, which contains a small quantity of a naphthol sulphonic acid (2.7). In the case of other ice colours tragacanth has been found a suitable adjunct to the naphthol solution. Finally, in the case of dianisidine blue, the addition of a copper salt to the preparation is essential, since otherwise the colour turns out a dull, fugitive violet. Naphthol D is used for dianisidine blue that is required to withstand the action of perspiration.

The pieces to be dyed are prepared by passing them 2 to 3 times through the naphthol solution, in a padding machine, the solution being preferably lukewarm. They are then squeezed very thoroughly, as otherwise the dye tends to rub off.

After the pieces have been padded with the preparation, they are dried, as thoroughly as possible, in the hot flue at a temperature of 70° C.; the better the drying, the fuller the resulting colour and the lower the tendency to rub off, though the use of high temperatures must be avoided or the naphthol will be vaporised. The goods cannot be treated with the preparation long in advance, but must be further treated as soon as possible afterwards—at any rate during the same day—or partial browning may ensue.

In preparing the diazo solution of the amine for the developing bath, the amine is dissolved in hot hydrochloric acid and water. It is then cooled by adding cold water and stirring in order that the sparingly soluble amine chloride may separate out in the finest state of division possible, because large crystals will not react so well in the subsequent treatment with nitrous acid.

Sodium nitrite, accompanied by lumps of ice, is next added, the nitrous acid of the sodium nitrite being liberated by the excess of hydrochloric acid and converting the amine into the corresponding diazo compound. Ten minutes, or even longer in some cases, should be allowed for the completion of diazotisation; the liquid is then filtered, and the hydrochloric acid, which would retard the coupling process, is neutralised by the addition of a cold solution of sodium acetate immediately before use.

In so far as the diazo solution contains an excess of free mineral acid, it is fairly stable, and can also be prepared without ice. After the addition of sodium acetate, however, it becomes readily decomposable, especially when it contains an excess of nitrite. Nevertheless, rather more than the theoretical quantity of nitrite must be used in order to obtain favourable conditions for diazotisation. It has also been found that the sensitiveness of a diazo solution increases with its concentration, and therefore strong solutions must be thoroughly cooled with ice, whereas this latter can be dispensed with altogether for dilute solutions. In this respect, however, the various amines differ considerably in their behaviour: some of them yield readily decomposable diazo solutions, whilst with others the diazotising is effected better at the ordinary temperature than in the cold. The Höchst azophore dyes, which contain the amines in already diazotised form, are very stable. Finally, it may be mentioned that the time required for diazotising varies, the developing bath for naphthylamine garnet, for instance, needing to stand a while before use.

To develop the dye, the naphtholised pieces are passed in the open form, through a padding machine containing the filtered diazo solution, which must be kept at constant strength by a continuous feed of fresh solution. The goods are then led over guide rollers, in the air, in order to allow the gradual coupling of the naphthol and diazo compound to attain completion. In the case of dianisidine blue, for example, this operation takes a long time, especially on heavy goods, and is very often irregular.

The pieces are then washed, preferably by a continuous process, the goods being passed in succession through a series of vats, in which they are first swilled and then washed in a stream of water.

Finally, the goods are soaped at about 60° C. (a little soda being added for red shades with a blue tinge), in order to lessen the tendency of the dye to rub off; and are then washed again.

In some cases these dyeings are coppered, the red being changed into a handsome fast tobacco-brown, whilst para-brown, for instance, is made much brighter.

The ice colours have two unfavourable properties to be kept in mind: they will not stand much rubbing or heat, the latter causing them to separate from the fibre by sublimation. The method of lessening the first-named drawback has already been described; but the only way to prevent sublimation—a property which is particularly noticeable in β-naphthol itself—is to guard the goods from exposure to any strong heat.

The dyeings—such as dianisidine blue—which are obtained by the aid of copper, however, are not sensitive to heat; and this blue will even stand the prolonged steaming necessary to develop the colour. The rest of the ice colours are only occasionally subjected to a short, gentle steaming when used, along with other dyes, in calico-printing.

Owing to its peculiar constitution, nitrosamine red can also be produced by bringing the two components on to the fibre at the same time, the material being entered in an alkaline solution of β-naphthol, nitrosamine, tragacanth, and Turkey-red oil. It is then dried, and left fourteen hours for the colour to develop.

In practice, however, the method pursued is on the same lines as with the other nitraniline preparations.

In the application of ice colours to yarn-dyeing, practical difficulties are encountered, which, however, have been overcome, more particularly with nitraniline red. This dye is used more especially when it is desired to maintain the soft texture of the yarn (knitting yarns).

Nitroso blue belongs to the colours produced by condensation on the fibre, but is only used in calico-printing.

Oxidation Dyes.—The colours developed on the fibre by oxidation include aniline black and paramine brown.

Aniline black is the finest and fastest black for cottons; and probably more work has been done and written about this dye than any other.

It is dyed on raw unbleached cotton; and can even be produced on dressed cotton, a method which has the advantage that the dressing does not cover the dye and mask its brightness.

Aniline black can be produced by the oxidation of an aniline salt in two ways, furnishing oxidation black and single-bath black respectively. The former and older method was first practised in calico-printing and subsequently applied to dyeing. The fabric is padded with a solution containing an aniline salt, an oxidising agent, sal ammoniac (as hygroscopic agent), and usually an oxygen carrier as well. After drying, the black is developed by chroming, soaping, and stoving or steaming. The aniline salt generally used is the chloride, which should be as pure (free from tolidine) as possible. The quantities employed in practice vary considerably, but about 100 parts by weight per 1000 represents the average—though a useful black can be obtained with even less.

The oxidising agent is chlorate of soda or potash, or both. The proportion (of the sodium salt) given in practical recipes is about 0·8 to 1 of aniline chloride.

For printing, copper sulphide or a salt of vanadium is used as the oxygen carrier. Vanadium may be replaced by cerium, which is said to give a finer black. (The preparation for this is made by treating cerite with sulphuric acid.) In dyeing, the same function is discharged by copper sulphate (1 to 2 parts by weight, per 100 of aniline). Of late the padding preparation for aniline black has been made with an admixture of acetate of alumina (130 parts per 100 of aniline), with the object of neutralising the hydrochloric acid and thus counteracting the tendency to turn green through the action of this acid on the fabric.

In preparing the padding liquor, the several ingredients are dissolved separately in water, and the solutions mixed together in the cold. In any case, the oxygen carrier should not be added until just before use. When copper sulphide is used, a thickening agent must be added to the solution to prevent that substance from separating out as a deposit. After padding, the fabric is dried at ordinary temperature and then either run through the Mather & Platt oxidation machine at the rate of 70 to 100 yards a minute, or else hung for a couple of days in a slightly damp atmosphere, at 25° to 30° C. (77° to 86° F.), to start oxidation—the former being the method in more general use.

The rapid oxidation apparatus of Mather & Platt, or, as it is generally termed for short, the "Mather-Platt," is a continuous steaming apparatus, and is largely used in calico-printing. In the view of this apparatus, shown in Fig. 26, *a* is an iron case of circular or quadrangular section, through which the goods *i*, from *h*, are passed over stretching rods *k*, *l*, and guide rollers *n*, *o*, in an ascending and descending direction, by means of the two sets of rotating rollers *b*, b_1, and are finally discharged through the same aperture above the rollers *p*, *q*, to be laid on the table *x* by the folding device *u*, *v*, *w*. The rate at which the goods are moved forward is usually regulated so that they remain in the apparatus about one minute.

Other details represented in the figure are 1, the steam admission valve; *y*, the perforated steam-pipe; *z*, a false bottom; 2, the waste steam valve; *g*, a small steam engine; *k*, a belt pulley; *f*, a fly-wheel; and *d*, a belt pulley, with the speed gear *o*.

The copper pipes situated at the inlet and outlet aperture for the goods are also heated with steam, to prevent wet stains arising from condensation.

The pieces placed in the oxidising chamber must be neither too dry nor too damp, since in the former case the colour develops badly and gives a dull brownish-black, and, in the other case, development goes on too quickly. The development of the black is retarded by draught or by too long a sojourn in the cold chamber, the reason for this being a partial volatilisation of the aniline and crystallising of the chlorate so that it can no longer oxidise. The piece turns a progressively darker green in the chamber owing to the formation of emeraldine, and when this shade has reached a certain intensity, further sojourn in the chamber is dangerous, the acid from the aniline salt rotting the fibre. On removing the pieces from the chamber the colour is developed by chroming, after which they are washed and finally soaped hot.

Chroming is effected in various ways, the amount of chromate used ranging from 1 to 10 parts per 1000 in direct relation to the depth of black required. A slight topping with direct (or indeed any other) aniline black has a very beneficial effect on dyeings of oxidation black, by lessening the tendency to turn green in course of time. For this reason it is preferable to combine the chroming with a topping dye, the goods being treated

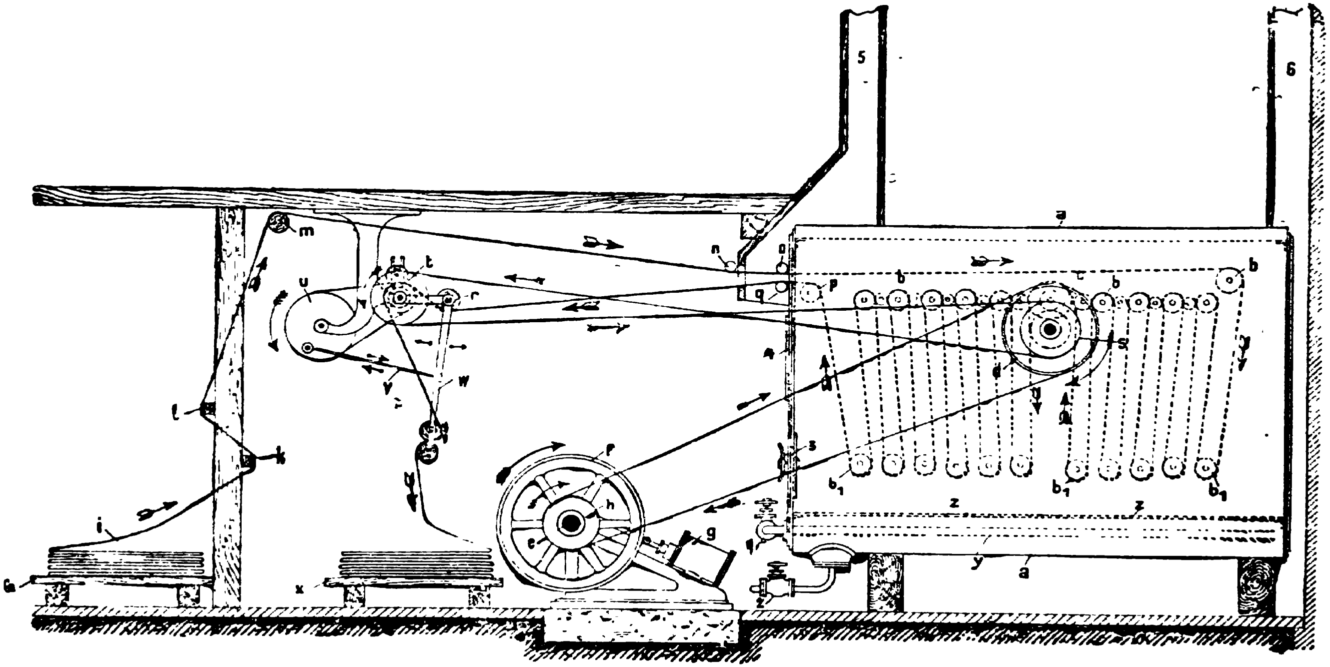

FIG. 26.

in a solution of bichromate and potash (7 per cent.), sulphuric acid (2 per cent.), and a little aniline (about $\frac{1}{2}$ per cent.),[1] for half an hour at 40° to 50° C. (104° to 122° F.) followed by a thorough washing.

In the introduction of oxidation black in yarn-dyeing, considerable difficulties had to be overcome; in particular, uniform oxidation in the warm chamber only became possible upon the construction of special reels on which the spread-out yarn is caused to rotate. Even until recently only a few works were able to dye yarn efficiently in this manner, and produce the so-called diamond black.

There are two disadvantages attending on oxidation black; in the first place, the hydrochloric acid of the aniline salt always more or less strongly corrodes the cotton fibre, and, where the work is carelessly done, this may extend to a complete rotting of the goods. The second drawback is that the colour turns green after a short time. This change on the part of aniline black apparently results from the formation of emeraldine by reduction, and is the more retarded the deeper the black. It is furthered by acids and by reducing agents, the chief among which, in practice, is sulphurous acid. In order to provide a remedy it is necessary that the black should be intense and well oxidised. By adding acetate of alumina to the padding preparation and employing a chrome bath containing aniline, a practically unchangeable black can be obtained. Another way of achieving the same result is by using "Oehler salt" (an aniline oil rich in m.-toluidine; but the black is rather browner than ordinary aniline black.

The liability of a black to turn green may be tested by suspending a sample of the fabric in a beaker containing bisulphite and sulphuric acid, covering the vessel with a watch glass. If the black does not become green within five to ten minutes, it may be regarded as permanent.

Frequently, in order to improve the colour and mask the change to green, the black is topped with methyl violet. Oxidation black is also produced on any silk goods in just the same way as on cotton, and is generally topped with methylene blue. Considerable advance in this branch has lately resulted from the introduction of the so-called Prudhomme's black. The *modus operandi* is similar to the later methods, except that potassium ferrocyanide is added to the padding solution. This salt reacts on the aniline chloride, forming aniline ferrocyanide and potassium chloride. It differs from the above-described oxidation black, inasmuch as the fibre is not corroded, the hydrochloric acid being combined with potassium, and that the development ot the dye proceeds more gradually: a great advantage in the production of printed goods. The quantity of potassium ferrocyanide depends chiefly on the amount of aniline, the average being about 50 grms. per litre (5 per cent. by weight) of padding solution; no oxygen carrier is required. The goods are first padded, then dried in a current of hot air by passing through a small chamber, and finally developed as in the older processes.

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[1] Referred to the weight of the cotton fabric.

Diphenyl black base I (Höchst) is paramidodiphenylamine. For dyeing, it is dissolved in acetic acid, and used in association with sodium chlorate (as oxidising agent), copper chloride or cerium chloride (as oxygen carrier) and aluminium chloride. Copper salts develop the colour sooner, but cerium salts give a bluer black.

After padding in the solution the colour may be developed by passing the fabric over hot cylinders, but a finer black is obtained by first drying in the hot flue and then developing for two to ten minutes in the Mather-Platt. Washing and soaping complete the process, chroming being not only unnecessary, but even unfavourable, owing to its effect on the tinge.

Diphenyl black has the advantage over ordinary aniline black of not being liable to turn green and not weakening the fibre; but it is dearer and is not very largely used. A cheap black, more closely resembling aniline black, is obtained with diphenyl black oil·DO (Höchst), a solution of diphenyl black base in aniline.

Diphenyl black cannot be used for dyeing Prudhomme black, the ferrocyanide of the base being insoluble.

Single-Bath or Direct Aniline Black has long been largely used for dyeing loose cotton and yarns, and more recently extended to cotton in warps.

Owing to its cheapness, it has suffered less than oxidation black from the competition of the sulphur and substantive dyes, and is still very important, especially since the discovery that its resistance to friction and fastness to light can be much improved by bottoming with substantive dyes, such as Congo-red, diamineral black, etc.

As the name implies, the dye is produced by dyeing the cotton in a single bath; this contains aniline chloride, potassium bichromate, and hydrochloric acid. Some dyers use, instead of hydrochloric, sulphuric acid, or a mixture of the two; and hydrofluoric acid has also been proposed for this purpose (Thiess & Cleff). Others again replace a portion of the chromate by copper sulphate.

The proportions of these reagents vary within wide limits.

As far as the aniline salt is concerned, the quantity depends entirely on the depth of black required, and therefore is limited by consideration of expense. In practice, for this reason, not more than about 11 per cent. of aniline salt or 8 per cent. of aniline oil can be used; even with 8 per cent. of the salt a very good black can be obtained. The average quantity of Bichromate is from 1·3 to 1·6 parts per part of aniline salt. Finally, the quantity of acid used differs so considerably in the various recipes that no average figures can be given. Nevertheless, it is irrational to employ more than 12 per cent. of hydrochloric acid; and 8 to 10 per cent. would generally be sufficient.

The dyeing process is performed as follows: The ingredients are dissolved separately, and mixed in a perfectly cold state just before use. The dye-bath should be as cool as possible, and used in a wooden vessel, the time of exposure being two to two and a half hours. The black will be less likely to rub off if the acid be added in several portions, and not all at once. The cotton is at first coloured green, then blue, and finally black. In order to utilise the bath better, the temperature may be raised to about 60° C. during the last half-hour. The more concentrated the bath the quicker will the colour develop. The chief point in this method is to secure the development of the aniline as far as possible in and upon the fibre, and as little as may be in the bath, since the black deposited in the bath adheres only loosely to the cotton, and easily rubs off. A good aniline black bath should therefore remain clear as long as possible, although, towards the end of the operation, a deposit is always formed in the bath.

On leaving the bath, the black is of an ugly brown shade, and must be improved by topping with logwood and hot soap. The logwood is fixed by the chrome deposited on the cotton whilst in the dye-bath.

All single-bath aniline blacks have a more or less pronounced tendency to rub off; they are, however, faster to acid than oxidation black, and do not corrode the fibre. The rubbing-off may be considerably diminished by careful washing, preferably in running water after dyeing. Finally, mention may be made of two modifications of this process. In the one, the single-bath black is produced in a warm bath containing less aniline than usual (about 8 grams per litre); the black, however, easily rubs off, and consequently this method is very seldom used. On the other hand, black is still produced on loose cotton by impregnating the material with a concentrated black bath, and then developing the colour by steaming. No advantageous method has yet been devised for recovering the chrome from the spent black baths.

Paramine Brown.—H. Schmid discovered that a brown colour can be developed, from paraphenylenediamine, on the fibre in the same way as black from aniline, the resulting dye being superior to that from manganese bistre owing to its simpler method of preparation and greater fastness to light and resistance to friction. Though mainly intended for printing—for which it is well adapted by reason of the ease with which it can be discharged (or reserved)—it can also be used with advantage in dyeing piece cottons. The dye-bath for this purpose is prepared by dissolving paramine (Badische) in water, a little rongalite C, sodium chlorate, sal ammoniac (both of these in equal amount to the paramine), tartar emetic dissolved in glycerine, and a little ammonium vanadate—all previously dissolved in water. For a full brown the solution should contain

1½ to 2 per cent. of paramine, the fabric being padded, dried at about 40° C. (104° F.) in the hot flue and developed in the Mather-Platt, followed by washing and soaping.

Mineral Dyes.—Of the mineral dyes developed on the fibre the following alone are of any practical importance: Manganese bistre, iron chamois, Berlin blue, chrome yellow, and orange chrome.

Manganese bistre is largely employed in calico-printing, on account of its fastness and the ease with which it is discharged. The goods are first padded with a solution of manganous chloride that has previously, to a slight extent, been converted into acetate by the addition of a little lead acetate. The concentration of the manganese solution is naturally in direct ratio to the depth of brown to be produced. Next, they are passed through boiling caustic soda of about 17° B. strength; then exposed to the air by passing over guide rollers, and, in the case of dark shades, returned to the soda bath. Finally, to ensure complete oxidation, they are treated in a hot bath containing about 1½ part, by weight, of potassium bichromate per 1000, and then washed.

Very good results can also be obtained with manganous chloride alone, or another organic salt of manganese instead of the acetate, though it is advisable, to secure equalisation of the colour, that part at least of the manganese should be in the form of acetate. The soda solution should be causticised beforehand with lime, since, if it contain carbonate, there will be formed on the material, in addition to manganese hydroxide, manganese carbonate, which is less easily oxidised and may give rise to irregularities in the colour. For light brown, the alkali may be weaker than that mentioned above. The padding with hot lye is effected in a steam-heated apparatus. In some works the final oxidation is performed with sodium hypochlorite, in the cold, instead of with bichromate.

Iron chamois is only sensitive to acids, being in other respects a very fast dye. The iron salt used is the so-called iron nitrate, or iron acetate, prepared from ferrous sulphate and lead acetate by double decomposition, the displacement of the sulphuric acid of the iron salt by the acetic acid being, however, incomplete.

The cheaper iron pyrolignite is not so suitable in this case, its tarry impurities muddying the colour.

Even ferrous sulphate does not give good results. The shade of the chamóis can be modified by adding aluminium acetate to the iron solution. The method of dyeing is as follows: The goods are padded with the iron solution, dried, then left twenty-four hours in the warm oxidation chamber, and afterwards treated, for the precipitation of the hydroxide, in a hot (80° C.) bath, containing about 1 per cent. by weight of chalk and 0·3 per cent. of water-glass (sodium silicate). Finally, they are washed, dried, and subjected to steam chemicking (see Calico-Printing), which gives the colour a more agreeable tone.

This method, however, is confined to the production of discharge effects in calico-printing, the following being that pursued generally in cotton-dyeing: The goods are passed in succession through an iron bath, a lime bath, and a chemicking bath containing "chloride of lime," these baths being contained in vessels similar to those used for the dunging process. After each bath a good squeezing is given to remove the superfluous liquor, and finally the goods are washed. This dye, however, has now been almost completely displaced by the substantive dyes.

Berlin-blue is a bright colour, fast to acids and light, and is still used, though only to a limited extent. The goods are prepared by passing them first through a bath of sodium stannate and then through sulphuric acid, after which they are washed and passed alternately through an iron bath and one of potassium ferrocyanide, until the desired shade is attained.

Chrome yellow and orange chrome are still largely used, both on account of their rich bright tone and because they increase the weight of the goods.

Chrome yellow is particularly fast to light, soap, and acids, though it is turned reddish by alkalis, and brown (lead sulphide) by sulphuretted hydrogen. The same applies to orange chrome, except that this dye is unaffected by alkalis and is stained yellowish by acids. The behaviour of these two pigments towards acids and alkalis is due to their ready conversion one into the other, chrome yellow being transformed into the basic chromate (orange chrome) by alkalis, whilst the latter is reconverted into the yellow normal chromate by acids. Both pigments are poisonous.

Chrome yellow is produced by depositing lead hydroxide or lead sulphate on the fibre, and then converting the compound into lead chromate by potassium bichromate. This is effected in different ways, especially as regards the fixing of the lead on the fibre. For instance, the goods are impregnated in a solution of lime, then treated in a solution of basic lead acetate, and then returned to the lime bath. Of course, a squeezing must be given after each immersion. The use of a basic salt of lead is explained by the chemical reaction, whereby the lime fixes the acid of the lead salt and deposits the hydroxide of lead on the fibre. Other dyers impregnate with a solution of a lead salt, dry, and then pass through a cold solution of ammonia (1 part to 6 of water) for two minutes. Again, the material is padded with a solution of magnesium sulphate, then dried, padded with a solution of basic lead acetate, and then left at rest for the formation of lead sulphate on the fibre. In any case, a good washing is given after the lead treatment, and the goods are then immersed in a solution of potassium bichromate (5 to 6 parts per 1000) at 50° C. for half an hour, and finally washed.

For the production of orange chrome, the chrome yellow generated on the fibre is "oranged" by treating the goods for half an hour in a boiling-hot bath containing 1 part, by weight, of lime per mil.

The Albumin Dyes are used only in Calico-Printing, and will therefore be described under that heading.

IV. Dyeing on a Manufacturing Scale.

Textile fibres are dyed on a manufacturing scale in the condition of loose material, rove, yarn, and woven fabrics, the latter being the most usual practice on account of the greater convenience and cheapness, it being possible to handle a larger quantity at a time with a smaller expenditure of dye, owing to the more closely compressed condition of the fibres. Dyeing the loose material is the most expensive form of all, there being a greater consumption of dye, and more waste during spinning and weaving, owing to the more extensive tearing of the fibres that have become more or less closely matted together in dyeing. Finally, it must also be borne in mind that some dyes, especially those produced by the aid of tin mordants,[1] increase the difficulties of the milling process. Consequently, the dyeing of fibres in the loose state is practised only in the case of better class single-colour fabrics, parti-coloured goods with woven designs, or in the production of yarns and fabrics from mixed fibres. By mixing together a number of loose coloured fibres, and then willowing, carding, and spinning the mixture, a series of shades can be produced that give the finished fabric the appearance of a uniformly coloured product. In this manner, by an admixture of white fibres with others dyed with dark shades fast to light, a faster light shade can be obtained than is possible by dyeing the whole in the same shade. (See Fastness of Dyes to Light.)

In dyeing loose fibres, perfectly soluble dyes and extracts alone are suitable. The vessels employed are generally hemispherical copper vats, the bath being heated by a steam coil under the perforated false bottom. Of late years there is a growing tendency to employ closed vessels, or open vats fitted with a circulation pump (Fig. 27).

All fibres are dyed in the condition of yarn, and that, too, more often than the loose state. The general practice is to dye in hanks or in warps, and latterly it has become the custom to also dye in the form of cops, especially in the case of cotton yarn.

Hank yarns are dyed in quadrangular wooden becks (Fig. 28) fitted with a false perforated bottom *b*, underneath which is situated a steam coil *d*, admitting steam to the bath. When, however, the volume of the bath liquor must not be allowed to increase during dyeing—for instance, in dyeing cotton with substantive dyes—a closed steam-pipe is used. The feed steam-pipe *e* must be separated by a wall *c* from the material to be dyed. The method of dyeing is as follows: The hanks *g* are first fastened together by intertwined strings to prevent tangling,

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[1] Such dyes are now seldom used.

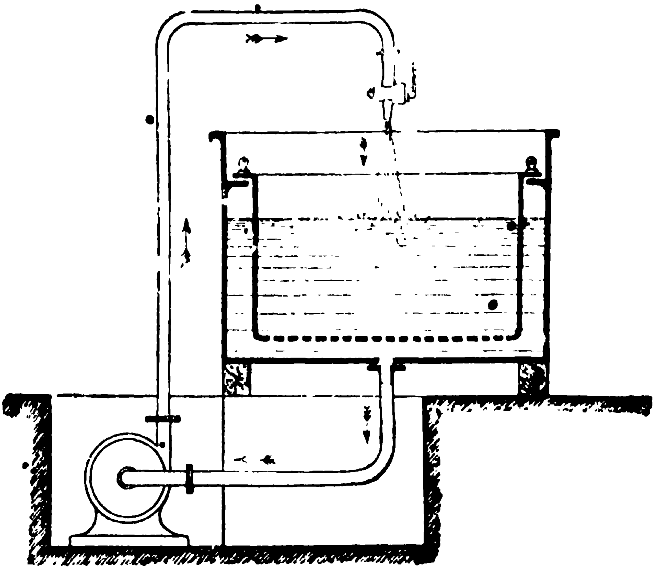

FIG. 27.

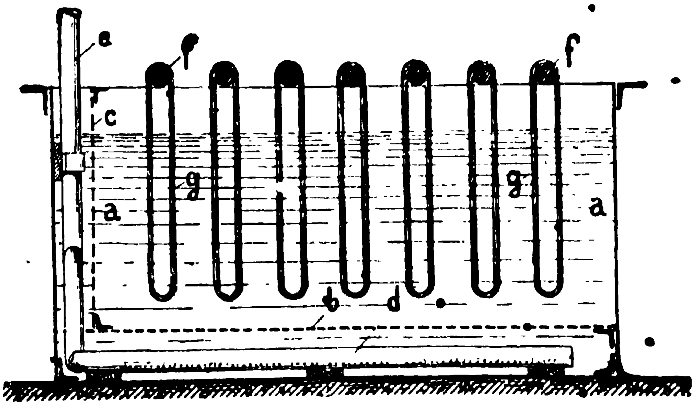

FIG. 28.

and are then hung in rows on smooth rods *f*, arranged crosswise on the edge of the beck. At intervals the hanks must be turned, a row at a time, by passing a rod through the whole row, lifting it out of the liquor, and giving it about a quarter turn. When it is desired to add more dye to the bath, the depending end of each row of hanks is laid over the adjoining rod. The movement of the bath liquor must not be more than a gentle undulation, in order to prevent tangling or felting in the case of woollen yarn. This defect is also minimised by reducing the period of exposure in the bath.

This method of dyeing entails a good deal of hand labour, on which account numerous hank-dyeing machines have been constructed wherein the yarn carriers are usually caused to rotate by means of toothed wheels, thus turning the yarn mechanically. It has the disadvantage that the prolonged handling of the yarn in the bath may easily cause felting in the case of wool. Other yarn dyeing machines, which either move the yarn intermittently through the bath (the Till machine), or raise and lower it automatically at certain intervals, are better; but the best results are still obtained by hand, as already described.

Worsted yarn is often dyed in the state of sliver, this condition being more suitable than that of loose wool. The sliver, having been slightly oiled, must be cleansed before dyeing, for which purpose it is steeped awhile in a very dilute warm solution of soda, then rinsed, and dyed after winding in hank form like yarn. The work must be performed with great care, since the sliver is easily torn and readily felts; the bath must not be boiling hot, nor may the material be worked about too rapidly. The advantage of dyeing in this form rather than in the state of yarn, is that any slight inequalities are unimportant, being eradicated during the subsequent spinning process. In dyeing warps, the yarn is led alternately up and down, over guide rollers, through several baths in succession. In order to protect the material, it is now largely the custom to dye the bobbins of sliver or carded fleece in dyeing machines, wherein a circulation of the bath liquor is maintained by suction and pressure, thus forcing the liquor through the material. A typical form of this class of apparatus is the Obermaier revolver shown in Figs. 29 and 30.

This machine consists of the vertical main cylinder *a*, around which are mounted in four horizontal rows a series of small

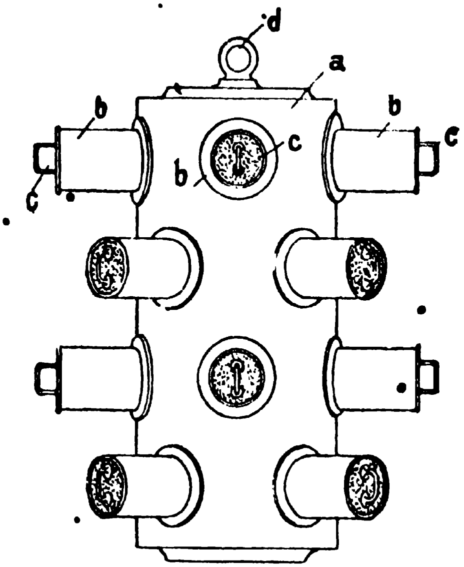

FIG. 29.

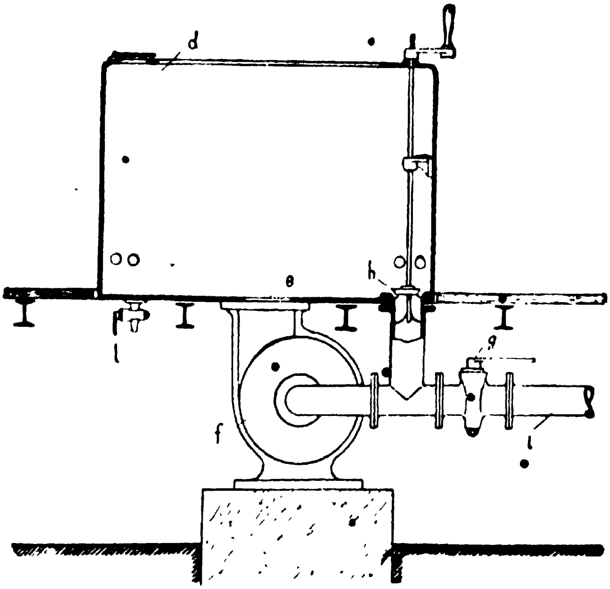

FIG. 30.

cylinders *b*, each containing a bobbin. At the junction of the bobbin cylinders with the main cylinder are a number of perforations, and similar perforations are made in the lids *c* of the bobbin cylinders. In dyeing, the cylinder is placed above the discharge pipe *e*, in the dye-vat *d* (Fig. 30), and the pump is started. The liquor is first forced by the pump into the interior of the main cylinder *a*, thence through the perforations into the bobbin cylinders, where it traverses the material, and thence escapes into the dye-vat. When the tap *g* is closed, the liquor returns to the pump through the raised valve *h*, and the circulation begins anew; when the valve *h* is closed and the tap *g* opened, fresh dry liquor, mordant solution, or water can be run in through the pipe *i*.

The vat is heated by steam-pipes, and is emptied by the tap *h*. This machine can be used for the various successive operations of damping, mordanting, dyeing, and washing, and also for drying the material by means of hot air. It is advisable to add only one-half the requisite amount of dye at first, then take out the bobbins when the bath is nearly exhausted, and reverse them so that those formerly in the top row are now in the bottom, and so on, the bobbins being also turned end for end in the cylinders.

When these mechanical dye-vats are used, the most soluble dyes should be selected, the materials should be as clean as possible, and the bobbins not too tightly wound.

Nowadays all these materials are often dyed in mechanical appliances.

Piece Dyeing.—The only time when this is a disagreeable operation is when the goods are defective and dirty. Many defects do not reveal themselves until after the goods are dyed, especially when the latter have to pass through a somewhat complex process of manufacture, as is the case with woollen cloth.

In such cases stains appear in the form of cloudy patches or as dark selvedges in full width dyeing, etc., and this most readily happens when small dye-vats are used, where the central portion of the piece is more compressed than the edges, which latter therefore absorb a larger quantity of dye.

A vat wherein all the operations of piece dyeing, such as damping, mordanting, and dyeing, can be performed in succession is shown in Fig. 31. In this apparatus heat is applied through a steam-pipe *l*, which is separated from the goods by a perforated partition wall *b*. This smaller compartment also serves for the introduction of the added solution of dye.

The pieces are sewn, end to end, in the form of an endless band, and generally reeled like a hank. If to be dyed wide open, the piece is kept spread out by the aid of a stick in the hand of an attendant whilst slowly passing through the dye. More frequently several sets of pieces are wound side by side on the same reel, and are kept separated by lattice partitions during their passage through the dye-vat, in order to prevent them from getting mixed on the reel. Cotton goods are dyed in the same way, mostly in hank form.

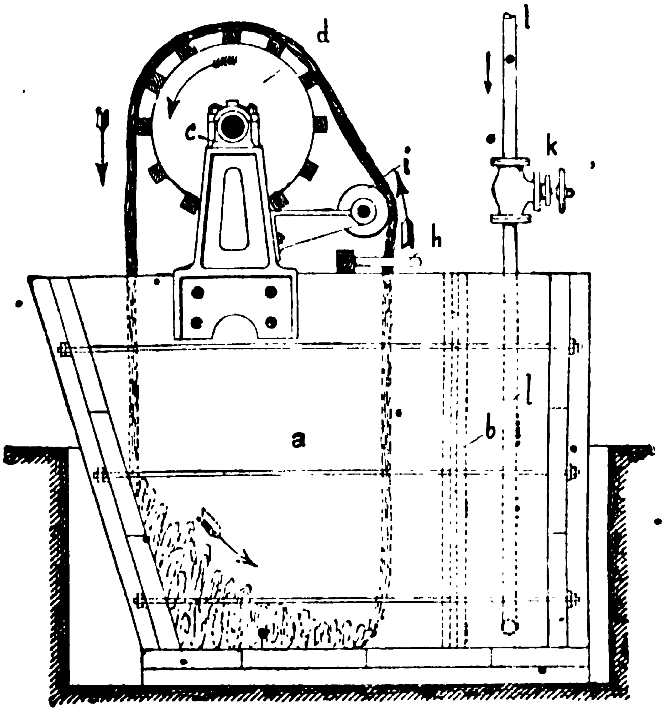

FIG. 31.

A machine largely used for dyeing piece cottons is the jigger, Fig. 32. It consists of a simple wooden vat *a*, on to which are screwed the cast-iron uprights *bcf* supporting the wooden rollers *de*. The goods, which are wound on the roller *e*, are drawn through the dye-bath in the direction shown by the arrow, when *d* is set in motion, and are then wound up on the roller *f*, which is mounted in a slotted bearing. The roller *e* is fitted with a loaded brake in order to keep the goods at the proper tension. If the goods have to be passed through the bath for several hours in succession, they are wound on *d* at first instead of on *f*. On motion being imparted to the roller *e* and the brake applied to *d*, the goods traverse the bath in the opposite direction, and are wound up on *e*. The jigger is the best machine for dyeing piece cottons with substantive dyes or basic dyes.

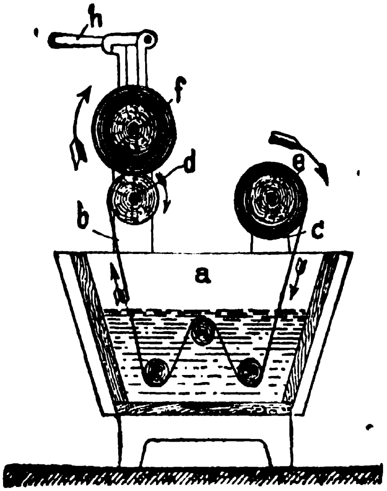

Fig. 32.

Before setting the dye-bath the water must be corrected or purified by boiling with soap or bran. The whole or a portion of the dye is then added. The usual method of dissolving the dye is to mix it into paste with a little hot or cold water and then suffuse it with a larger quantity of hot water, pass it through a linen filter, and run it into the vat; the undissolved residue is brought into solution by a further addition of water. As a rule, it is not advisable to place the solid dye-stuff in the vat. Distilled or condensed water should be used for dissolving dyes; in the case of basic dyes, a little acid facilitates solution, whilst soda is often useful as an adjunct in dissolving acid dyes. Dyes in paste form must be carefully stirred up with water.

After dyeing, the goods are generally rinsed, to remove adherent impurities and dissolved dye. Loose materials are rinsed in rinsing machines; yarns in the hank are usually hand-washed in the dye-vat, the dye liquor being drawn off and replaced by fresh water. There are also yarn-washing machines, wherein the yarns are suspended from revolving rollers. Washing in running water is the most efficacious. Piece-goods are washed on the reel; in the case of fugitive dyes the pieces are passed wide open through becks fitted with rollers. Owing to the multifarious character of the operation, it is impossible to go further into details.

The dyed goods are drained in the hydro-extractor. Drying is effected, in the case of loose material, in special forms of apparatus, frequently by the aid of hot air in carbonising machines. Yarns and piece-goods are dried by hanging in warm chambers; piece-goods more frequently in revolving cylinders, stretching frames, and calendering machines, similar to those used in the finishing process.

Dyeing in Mechanical Appliances.

In the foregoing description of the appliances used in dyeing particulars have been given of several in which hand labour has been more or less completely replaced by power; but the term "dyeing machine" is reserved for appliances in which the bath liquor is caused to circulate through the fibrous materials by suction or pressure. The apparatus shown in Fig. 27 therefore belongs to this class.

Of late years machine dyeing has been greatly extended, and the number of patented appliances has become so large that only a general review, coupled with a few examples, can be given.

Cotton is now dyed by machinery, in the condition of "flock" or waste; also as sliver, slubbing and rove, hanks, beamed warps, and to a very large extent as cops and yarn. Wool is dyed loose (for woollen yarn), as sliver (for worsted yarn), cops, quick-traverse bobbins, and most of all as yarn.

The machines may be of open or closed type. The circulation of the dye liquor is maintained by pumps, gas pressure or suction, steam pressure, vacuum, and centrifugal force. Vacuum and steam pressure are employed with sulphur and vat dyes from which it is desirable that air should be excluded.

The dye-stuffs used must be readily soluble in order that no solid matter may be deposited on the material, and to facilitate the process. Consequently, basic and mordant dye-stuffs are not suitable for machine dyeing; nevertheless, cops are dyed Turkey-red, though the work is only carried on in one establishment.

Both the material to be dyed and the water used should be quite clean, to prevent the risk of any precipitation on the fibre. Even the presence of lime (in very hard water) may in some cases result in spotting (precipitation of the lime by the alkali in the bath), for instance in washing goods that have been dyed with sulphur dyes. For similar reasons, copper and chromium should not be used together in the after-treatment of sulphur dyes.

Broadly speaking, the advantages of dyeing by machine are as follows: protection of the material, which is kept soft and open; possibility of using stronger dye liquors, thus saving steam, water, and dye; and the reduction to a minimum, or entire suppression, of slow and costly hand labour. Machine dyeing is particularly valuable for treating cops, the spinning frame being so arranged as to build the yarn automatically into the form in which it is most suitable for weaving. To dye the yarn in hanks it must be reeled, dyed, and then re-wound into cops, a method entailing much hand labour and involving increased risk of breakage.

Further advantages of these cop-dyeing machines are their higher working capacity, and the possibility of employing softer yarns, which therefore fill up the fabric better.

Dyeing machines are mostly made of copper, iron being used for sulphur dyes. The chief point to be considered in their construction is to ensure uniform resistance throughout to the dye liquor circulating through the fibrous material, in order that all parts of the latter may come into uniform contact with the dye. If this condition is not fulfilled, irregular dyeings may easily result.

The machines may be divided into two classes: pack machines and skewer or carrier machines. The running costs of both kinds are about the same, but the former type can deal with larger quantities at a time and allows stronger dye liquor to be used (about 1 : 3 as compared with 1 : 10). The pack system is the more widespread, but the carrier system is the better, being free from the great drawback of the pack system, *viz.* the necessity for using packing material. Moreover, the cops cannot be forced out of shape; less motive power is needed, the liquor being able more easily to penetrate the thin layers of material and dye them right through; and dyeing to match shades is easier, the machine being usually open, and thus enabling a sample to be taken out for inspection without hindering the work.

Finally, the pack system offers the advantage that the dyed cops can be drained on the spindles (*e.g.* by aspiration), thus assisting oxidation in the case of the sulphur dyes. This cannot be done with the pack system, centrifuging being necessary.

On the other hand, the carrier system has several drawbacks, including the fact that one is restricted to a definite form of winding, and the machine is liable to work irregularly through the holes in the spindles getting clogged up. The cops have to be skewered very carefully by skilled labour, or a good deal of waste may result, especially when the noses of the cops are readily damaged.

In working the pack system, the chamber of the machine is first lined with a soft cotton fabric (molton), which of course must be thoroughly clean, a special cloth being used for each colour. For light shades and for dyes which are difficult to equalise (*e.g.* blue sulphur dyes), the cops are packed under strong pressure. A general rule is to pack the edge highest. When wool is being dealt with, it must not be forgotten that this material swells up in dyeing. Loose wool, too, must not be too firmly pressed or its spinning properties will be impaired.

In cop dyeing, the form of the spindles or skewers, and the kind of material of which they are made, play an important part. Spindles of the sectional shape represented in Fig. 33 are found to answer very well. They may be made of rubber, wood, iron, lead, brass, etc. Rubber is expensive, and only the best quality should be used. If wood be employed, separate spindles must be used for each colour, because the wood itself gets stained. Hard wood is the only really suitable kind. The general use of metal spindles is frequently precluded by the character of the metal, brass being unsuitable for sulphur dyes, and iron for acid liquors. Lead is generally an advantageous spindle material, being flexible and also easily cleaned with sulphuric acid. But, as it marks the material with which it is placed in contact, it cannot be used in dyeing light colours.

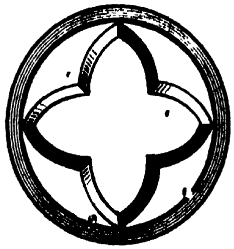

Fig. 33.

The paper of the shells on which the cops are wound, must not be coloured or loaded, and must contain as little size as possible.

In machine dyeing, the readily soluble acid dye-stuffs are well adapted for wool, and most of the substantive dyes for cotton. The method is also favourable for dyeing with sulphur dyes, because, in such case cheaper machines, of iron, can be used. A perfect result, however, is difficult to obtain, and is possible only when the oxidation of the dyeing is not allowed to proceed too quickly.

The Mommer Cop-Dyeing Machine.

The principle of this apparatus (Fig. 34) is as follows: The cops to be dyed are formed into a block which presents the same resistance in every direction to the bath liquor. This block, *a*, is formed by placing together a number of frames in which the cops, mounted on heavy spindles, are arranged in parallel rows. Each frame then represents a porous wall of cops, through which the bath liquor can penetrate without difficulty. The block is placed between the two perforated partitions *c* in the closed air-tight chamber *b*, into which the bath liquor is forced by the pump *e* from the vat *d*, through the pipes *f g*, according to the way the taps *h i* are set, so that the liquor traverses the block either from right to left or *vice versâ*. In the position of the taps as shown in the figure, the liquor passes through the tap *h* into the chamber *b*, traverses the block *b*, and returns through the pipe *k* to the dye-vat *d*. The taps can also be set so that the liquor enters the chamber *b* through the pipe *g* and the tap *i*, and, after traversing the block of cops *c*, escapes through the tap *h* and pipe *l* to the vat *d*.

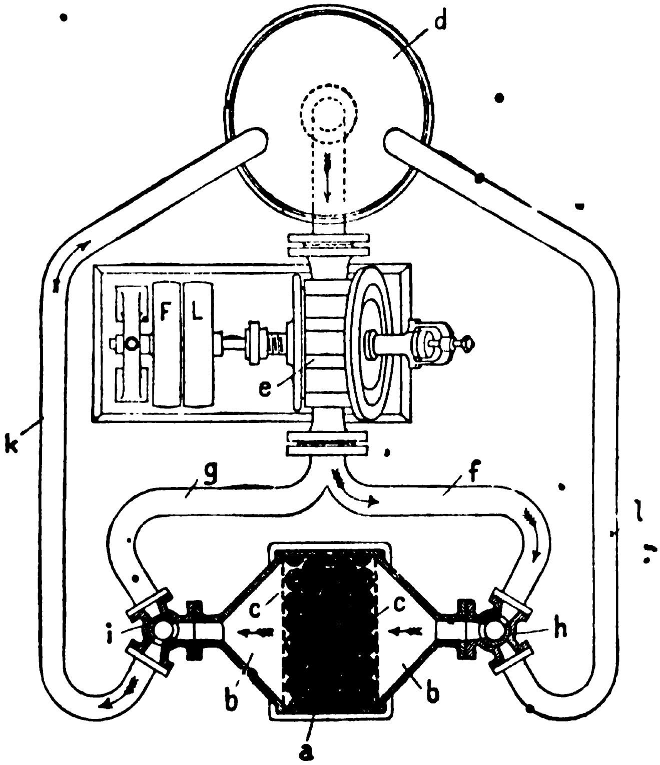

Fig. 34.

Froth Dyeing.

Mention may be made of a special method of dyeing introduced by C. Wanke of Zwickau, who found that slivers which cannot be dyed by immersion in hot dye-baths will take the dye well if entered in the froth of a soapy bath liquor. Apparently, the film enveloping the bubbles of froth absorbs the thin stratum of air and water in contact with the surface of the fibre, and thus enables the dye solution to penetrate.

The Selection of Dye-Stuffs for Dyeing.

The kind of dye-stuffs to use for producing a particular colour depends both on the nature of the fibre and on the form in which it is to be dyed, and finally also on the requirements exacted of the colour itself.

Cheap dyes will be chosen for cheap goods, and dyes fast to light for goods that will have to be exposed to the light a good deal. In dyeing loose wool the prime consideration is fastness to milling on the part of the dye, whilst in dyeing yarn and piece-goods the equalising properties must chiefly be borne in mind. In short, the dyer must not only be in a position to produce a given shade of colour in dyeing, but he must also have an accurate knowledge of the behaviour of the various dye-stuffs and their combinations towards the influence of light and the various other agencies (see Tests for Fastness) that may have to be encountered.

Silk-Dyeing.

Silk is dyed in the hank form almost exclusively, very rarely loose. Hand in hand with this operation goes that of loading, which is almost the more important of the two.

It is only in exceptional instances that special requirements in respect of fastness are exacted of silk-dyeings. The dyes most suitable for the purposes of the silk-dyer are those enabling him to produce all imaginable shades of colour in a rapid and easy manner, with perfect equalisation, the chief qualities being good capacity for equalisation and combination. In comparison with wool and cotton, the number of dyes employed is remarkably small, and these mostly belong to the group of acid dyes, the following being most in use :—

Greens: acid green, malachite green, milling green BW (Lo.), alizarine cyanine green (By.).

Yellows: quinoline yellow, citronine, azoflavine S, Indian yellow, thioflavine T, chromine G: naphthol yellow and picric acid are often employed for shading in the brightening bath.

Orange: orange II, 2R, T, GT, IV; croceine orange, eosine S (ex. yellow).

Brown is almost entirely obtained by the combination of suitable colours.

Reds: Several ponceaus, croceine scarlet, azogrenadine, eosamine, fast red, Bordeaux, cloth red, azofuchsine, acid fuchsine, irisamine, rhodamine, phloxine, primrose, Magdala-red.

Violets: acid violet, methyl violet, formyl violet, Victoria violet.

Blues: alkali blue, marine blue, methyl blue, patent blue, cyanol, formyl blue, Victoria blue, new Victoria blue, alizarine saphirol, alizarine astrol, induline.

Of these the most suitable for combination are citronine, orange II, fast red, rhodamine, phloxine, methyl violet methyl blue, and marine blue.

Colours fast to water are obtained from citronine, roccelline, and marine blue, by solidification after dyeing.

For colours to stand soap, the dyes most frequently used are a few alizarine reds (powder), alizarine orange, cœruleine, galleine, and a series of other mordant dyes which have already been mentioned, and, as stated, can in many cases be advantageously replaced by substantive and sulphur dyes.

Black, the most important dye for silk, is mostly obtained with logwood and also to some extent with other dyes, such as naphthylamine black 4 B, or Diaminogene B (C, diazotised and developed).

Wool-Dyeing.

Wool is dyed in the loose state, as sliver, yarn, and in the piece after weaving; sometimes also in two stages of manufacture, *e.g.* by vatting in the loose state and topping in the piece.

Of all fibres wool is the hardest to damp, and is therefore best dyed at boiling-heat. Consequently, dyeing in the vat, an operation performed at medium temperatures, affords a very sharp test as to the capacity of any sample of wool for absorbing dyes.

The chief dyeings for wool are blue, red, and black. A very large number of dyes, singly and in combination, are used, the most popular and suitable of which will now be described, without any claim being made to absolute completeness.

Green.—A number of bright shades, bearing the name "billiard green," are produced on woollen cloth. Formerly these were obtained from fustic, indigocarmine, and alum (in a single bath), but nowadays acid green, cyanol green, or patent blue is used along with some yellow dye, such as quinoline yellow, fast yellow, tartrazine, etc. A particularly pure green is furnished by patent blue N and quinoline yellow.

Washing greens are produced from brilliant milling green B (C.), fast acid green (M.L.Br.), diamond green 3G, B (By. for dark shades); from patent blue and milling yellow O (C.); anthracene blue WG extra, and alizarine yellow GGW, or mordant yellow; latterly also with alizarine saphirol, alizarine pure blue, or anthracyanol R, as blue components; finally also with alizarine cyanine green (By.).

A series of dull olive-green tones are produced by combinations of red, blue, and yellow, *e.g.* with chromotrope, azo acid yellow, and patent blue; or with ponceaus, a yellow and acid green; or, finally, with fustic and logwood.

A very dark, almost black, fast green is obtained by dyeing the loose wool with fustic and alum, and then vatting; or by dyeing with diamond green BSS, or alizarine viridine (suitably shaded), followed by chroming.

Yellow.—Bright shades of yellow are obtained with quinoline yellow, naphthol yellow, tartrazine, the fast yellows, etc.; all these dyeings, however, are incapable of withstanding washing, and, except the two last named, are fugitive to light. They are employed for equalising (trimmings for uniforms) and for many yarns. Faster dyeings are obtained by means of milling yellow O (C.), sulphone yellow, and with quercitron, or flavine, on tin-alumina mordants. The two latter dyes reduce the milling fastness of the wool. A beautiful yellow that will completely withstand carbonising can be produced by dyeing with alizarine yellow GGW (M.L.Br.) and potassium bichromate in a single bath.

Anthracene yellow C (C.) gives a very clear yellow, of greenish tinge, furnished by dyeing in an acid bath and then treating with chromium fluoride.

A series of dyeings more or less fast to milling can be obtained with alizarine yellow 5G, chrome yellow, diamond yellow, salicine yellow, Domingo chrome yellow, milling yellows G and R (Leonhardt), chrome fast yellows G and 2G (Soc. Chem. Ind., Basle).

Dull greenish-yellow colours are produced on loose wool by galloflavine, or cœruleine and fustic, on chrome mordant; on yarns and piece-goods by an orange and an acid green (fast to alkali) or blue.

Orange is produced with one of the orange acid dyes, or with a ponceau and one of the yellow dyes already mentioned; with sulphone orange, or milling yellow O and diamine scarlet. For fast dyeings, cochineal and flavine were exclusively used at one time on tin mordants; if duller shades are desired, flavine is replaced by quercitron, and a tin-alumina mordant is used. Alizarine orange G, GG, and W, will also stand milling fairly well.

Reds.—The chief shades of this important colour are scarlet and madder red (a duller brownish-red). For fast scarlets use is made of cochineal on tin mordant; for fugitive kinds, the various ponceaus and croceine scarlets. A bright red is obtained with rhodamine and an orange dye. Madder shades are produced with fast red, cloth red, naphthamine fast red H, anthracene red, anthracene chrome red H, chrome fast red, and with substantive dyes, the fastest kinds being obtained from alizarine.

It should be mentioned that considerable divergence exists in the fastness of the various ponceaus, a circumstance still insufficiently known and appreciated in practice. Some of these dyes are just as fast to light as cochineal; but without exception their fastness to milling is not good, since all of them bleed into the white during that process, though even in this particular differences exist. All of them have a greater capacity for penetrating the fibre than cochineal—the palatine scarlets in particular.

The fastest to light of all the ponceaus are the palatine scarlets (B.A.S.F.), the Victoria scarlets (M.L.Br.), brilliant ponceaus, 4RS, 3R, 4R (C.), a few marks of brilliant croceine (C.), croceine scarlet R (By.), croceine 3B, RX (By.), etc. The palatine scarlets are identical with dyes sold under other names; palatine scarlet A, for example, being the same as Bayer's cochineal scarlet PS and Cassella's brilliant cochineal. Those furnishing the more bluish shades are ponceau B extra (M.L.Br.), scarlet B (By.), new red 5R (By.), a few B marks of brilliant croceine (C.), etc.; ponceau B extra and scarlet B being the best as regards milling fastness. These two can be used for goods that are to be milled, but must then be dyed by the aid of tin chloride and potassium bitartrate; and the milling must be conducted with care. Colours that will stand sulphur are furnished by *e.g.* ponceaus 2R, 3R (M.L.Br.), and the cheap double ponceau 4R (By.).

The best means of producing, on loose wool or yarns, colours that will not bleed into the white when milled, is by the employment of a red substantive dye. The most suitable for this purpose are: delta purpurine, diamine scarlet (dyed with ammonium acetate and acetic acid), fast diamine red, emin red, benzo fast red, fast scarlet (By.), milling scarlet 4RO, 4R, conc. (M.L.Br. dyed with acetic acid). Many of the substantive dyes, like delta purpurine, fast diamine red, etc., are also fast to sulphur, an essential condition for goods that are to be sulphur-bleached.

The fastest red on wool is produced by means of alizarine (powder) on a mordant of alumina, chrome, and tin. For a madder red these mordants are used in the following proportions:—

Alum	12 per cent.	
Tin salt	1½ ,,	
Potassium bichromate	1 ,,	
Potassium bitartrate	4 ,,	
Oxalic acid	4 ,,	(with water of about 20° of hardness).

A colour of the same appearance can, it is true, be obtained with alumina and alizarine alone, but is not thoroughly fast to milling, though it may be rendered so by dyeing with addition of calcium acetate, tannin, and soap (B.A.S.F.).

Austrian cavalry trouserings are dyed a fast milling red with anthracene yellow, topped with this indigo red.

Of course this by no means exhausts the list of red dyes applied in practice to wool, other shades (crimsons) resembling fuchsine, of a fugitive character, being produced on piece-goods with fuchsine, fast ones with fast acid violet A2R (M.L.Br.), or cheaper ones with azo acid fuchsine and similar dyes. This indigo red B gives fast shades.

Rose Red is applied only to woollen yarns and piece-goods, the dyes used being cochineal, with tin mordant, rhodamine—and also other eosines, when the shade requires. Diamine rose (C.) is also suitable for this purpose.

Alizarine rubinol R (By.) can be recommended for fast dyeings.

A series of red dyes are used for combination dyeings, the chief consideration being their levelling properties. Azocarmine is a red which dyes evenly, but has been displaced to some extent by azo fuchsine G (By.), although the latter cannot resist alkalis. If a red that will dye level below boiling-point is required, azo acid violet (By.) is taken for bluish shades; Bayer's azogrenadine L, naphthol red or Victoria rubine (Hochst); or Dahl's azocoralline, for yellow shades.

Other even dyeing reds used for combined work are: chromotrope (fast to light), azocardinal G (Akt.), Guinea red 4R (Akt.), and the very fast alizarine rubinol (By.).

Bordeaux is produced, as a dark shade, fast to milling, on loose wool and on yarn by means of alizarine and chrome mordant. This colour bleeds slightly, but can be improved in this respect by adding copper sulphate to the mordanting bath. In piece dyeing this colour is mostly obtained with aniline dyes, various fast reds—among which special mention is deserved by the extremely powerful fast red O (M.L.Br.) and the cheaper fast red NS (By.)—or with the acid of levelling dyes like chromotrope, azocarmine, etc. A Bordeaux very fast to light can be obtained with alizarine rubinol B (By.).

A bright Bordeaux, very fast to light, can be obtained by the aid of fast acid violet A2R (M.L.Br.), chromotrope 2R, orange C, and a blue.

A Bordeaux that is faster than can be obtained from aniline dyes, and of a shade not obtainable with alizarine dyes, is furnished by mordanting with alum, tin salt, and potassium bitartrate, dyeing with cochineal and madder, and darkening with archil according to requirements. This combination, however, is now very seldom used.

Blue.—This is perhaps the most important of wool colours, and is produced in a variety of ways.

For medium and dark blues, indigo is the first dye to be considered, because it furnishes the fastest dyeings, or the so-called "fast blues". The wool is dyed in the vat both as loose wool, yarn, and in the piece, though, owing to the difficulty of obtaining proper equalisation by this last means, it is a general custom to blue wool in its loose state. "Semi-fast blue" is produced in two ways, the vat-blued pieces being either boiled with santal, or first mordanted with alum, copper sulphate, and bitartrate, and then dyed with logwood, as already described. The blue obtained with the aid of sandars is much faster than that topped with logwood. Vat blue, topped with thioindigo red B, gives a fast blue with reddish tinge. Vat blue is also frequently topped with methyl violet or an aniline blue, to improve its brightness, or bottomed with azofuchsine (By.) or fast acid violet R (M.L.Br.) to save indigo.

Wood blue, which was formerly very popular for dyeing in the piece, has largely gone out of use by reason of its fugitive character, being replaced by the anthracene blues (especially WG ex.), the alizarine cyanines, alizarine blue, brilliant alizarine blue (By.), sulphocyanine, anthracene chrome blue, fast mordant blue B (M.L.Br.), salicine blue (Kalle), various fast blues, brilliant cloth blue (Kalle), lanacyl blue (C.), Domingo blue R (L.), etc. Other dyes employed for bright blue are, brilliant milling blue R (C.) and milling blue 2R ex. (M.L.Br.): which, when used with acetic acid, give dyeings that will stand milling well.

The anthracyanines (Bayer) are very fast to light, and dye level; and their properties are often mutually complementary, so that one may suit one particular purpose whilst another may prove better adapted to meet different conditions. For example, sulphocyanine gives indigo shades that will stand wear, but not steaming.

A number of blue dyeings, known under the names "navy blue," "Tegethoff blue," etc., are most easily produced with acid violet and acid green, or faster with logwood, acid violet, iron and copper mordants, and oxalic acid, in a single bath. Indulines are also used in combination with logwood, by mordanting as for wood blue, and then dyeing.

The so-called "potash blue," formerly produced with logwood and ferrocyanide, is now most frequently dyed with patent blue, acid violet, and a small quantity of orange.

Bright light blue dyeings are produced—generally on yarns—with alkali blue, or the somewhat faster (to milling) alkali violet, whilst perfectly milling-fast blue is obtained by combining alkali violet and milling yellow O (C.). Lighter tones are preferably produced with Victoria blue, or, if required somewhat greener, with patent blue, etc.

A number of dull pale blue to grey shades, known as "pearl," etc., are dyed with patent blue and an easily equalising acid violet, and, if necessary, shaded with yellow. In the case of alizarine blue, anthracene brown, cœruleine, etc., are used for shading, the same dyes being used for shading after alizarine cyanines and chromium fluoride in a single bath; also by blueing in the hyposulphite vat or thioindigo red B; and topping with alizarine cyanines and chromium fluoride, with alizarine saphirol, with fast acid blue R (M.L.Br.); less fast dyeings with patent blue or with indigocarmine and archil (rarely nowadays), etc. Similar fast shades are obtained with alizarine blue-black B and 3B, and with anthracene chrome blue, toned with acid anthracene brown.

On loose wool a fast grey, of a shade unobtainable with alizarine dyes, is produced by blueing in the vat, topping with fustic and sumach, and darkening with iron.

Violet is met with either as very vivid violet or as purple. Bright, but fugitive, dyeings of this class are produced with methyl violet or acid violet; darker, duller, and faster shades with galleine, lanacyl violet, fast acid violet, or alizarine Bordeaux, and the fastest of all with alizarine and alizarine blue on chrome mordant.

So-called purples are most frequently produced, on piece-goods, by topping vat blue with chromotrope or a ponceau, or with cochineal and alumina-tin mordant. These dyeings are also frequently produced on yarns and piece-goods with an acid violet or a good equalising red and blue dye.

Drab.—This colour is obtained solely by the combination of red, blue, and yellow, a distinction being drawn between aniline drab, alizarine drab, and dye-wood drab, according to the class of dye used.

Though deficient in fastness, the aniline drabs exhibit special advantages for piece dyeing, and play a great part in that branch. Their chief superiority consists in the ease with which the desired shade can be obtained, and in the possibility of dyeing in a perfectly uniform manner goods that are impure or contain different wools, more satisfactorily than with alizarine or wood dyes. Only such dyes as equalise well are used for this purpose, most frequently the following: 1. *Reds.*—Azofuchsine, azocarmine, lanafuchsine, archil N (C.), azogrenadine S (By.), azoarchil BB (C.), amidonaphthol red (M.L.Br.), monopol acid red 4B, azophloxine 2B (By.), alizarine rubinol (By.), etc. 2. *Yellows.*—Fast yellow, lightproof yellow (By.), acid yellow AT (C.), quinoline yellow, tartrazine, azoyellow and allied yellow, together with various acid orange dyes. 3. *Blues.*—Patent blues and cyanines, cyanol, fast green (blue tinge—By.), wool green S (B.A.S.F.), cyanol green, fast cyanol green (C.), alizarine saphirol B, SE, alizarine astrol, alizarine emeraldol (By.), etc.

Up to within recent years, drabs to stand light could not be produced with acid dyes, because the dyes themselves were not in existence. True there were several fast reds and yellows, such as: chromotrope, azofuchsine, fast yellow, and tartrazine; but, for blues, only the fugitive greens and blues of the triphenyl-methane series were available. Now, however, there are numerous very fast blues of the anthraquinone series well adapted for this purpose. For example, a very fast drab is obtained by dyeing with alizarine rubinol B, lightproof yellow and alizarine saphirol.

Aniline drabs are liable to change their colour, more especially when the yellowing has been effected with an orange dye. The combination of chromotrope, cyanine or cyanol, and a yellow like azoyellow, least exhibits this tendency, and is also advantageous in other respects. Another peculiarity exhibited by light drabs is the phenomenon of "insolation," whereby the yellow entirely disappears on exposure to strong light, and thus alters the shade completely. In the dark the original colour reappears. This peculiarity is probably due to the fact that the goods become drier in the light, and is especially noticeable in the case of fast yellow and metaniline yellow.

The paler wood drabs (with logwood, fustic, and redwood) are mainly produced in the wool, by the single-bath darkening method. For dark shades, wood drab is previously mordanted with chrome; but this is seldom practised, since the dye makes the fibre hard. Finally, alizarine drab is most frequently employed for fast drab in piece dyeing, and for dark drab shades dyed in the wool. It is produced by mordanting with chrome and dyeing with anthracene brown (suitably toned with other mordant dyes); or by the single-bath method (followed by chroming) with anthracene acid brown (C.), acid anthracene brown (By.), or acid alizarine brown (M.L.Br.); by combining anthracene chrome red or acid alizarine red, with anthracene yellow, diamond flavine, mordant yellow and anthracene chrome blue, acid alizarine green G (M.L.Br.), or alizarine blue-black (By.).

Brown.—For piece dyeing and hatting felts anthracene brown is still largely used; but for loose wool and yarn, acid anthracene and acid alizarine browns are mostly employed. Cassella's anthracene chrome brown SWN is distinguished by fastness and level dyeing.

In piece dyeing the production of wood brown, finished by darkening is still largely practised. For the reasons named in connection with drab dyeings, the last-named dye is unsuitable for loose wool; it is, however, still used, though santal must be replaced by alizarine orange (eventually by alizarine red or cloth red). The same aniline dyes that are used for drab also find employment for brown-dyeing piece-goods.

Black.—For the production of this important colour, the following shades and dyes come under consideration: Logwood, various acid blacks and a whole series of black mordant artificial dye-stuffs, all of which are fixed on the fibre by after-chroming (with or without addition of copper sulphate).

The logwood blacks differ considerably as regards their fastness to light, according to the method of production employed; chrome black is fast to acids, but not to light, though in this respect it is improved by the addition of copper sulphate; iron black is specially fast to light, but very sensitive to acids. As a rule, the logwood blacks have a great tendency to rub off. Iron black still remains one of the best blacks for wool, on account of its excellent equalising powers, covering power, and fastness to light. In some instances it is impossible to dye dirty and nopped fabrics black except with logwood; and few of the above-mentioned dyes can equal it in fulness and beauty of colour. In the case of very dense shades, however, logwood gives a rather brownish-black, and better results are furnished by naphthylamine black 4B.

Logwood is still largely used, especially as chrome black, in dyeing yarns and as a single-bath black in piece dyeing.

The black acid dye-stuffs, such as naphthol black, naphthylamine black, etc.—most of which are fast to light[1]—are largely used on account of the simple manipulation required and the fact that careful washing after dyeing is unnecessary; and they are more particularly employed for piece-goods containing cotton threads which are desired to remain white after dyeing. For the most part, however, they do not sufficiently resist milling, and many of them are only used on account of their cheapness. Naphthylamine black 4B and Biebrich patent black 4AN, 4BN, find extensive application. Fine worsted suitings are often dyed with naphthyl blue-black N (C.) combined with sumach extract, copper sulphate and ferrous sulphate. Latterly, however, these dyes are used far less, better-class goods being mostly dyed with diamond black and other black mordant dye-stuffs.

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[1] The opinion held in practice that all these acid blacks are equally fast to light is incorrect, many of them, such as palatine black, azo acid black, etc., being fugitive.

In the dyeing of loose wool and yarns, the handsome iron black was the first to be displaced by other blacks, such as logwood chrome black, diamond black (By.) and alizarine black (B.A.S.F.), because it hardened the fibre. Diamond black has now been admirably supplemented by the introduction of the marks PV, PVB, P2B, which are distinguished by their fastness to "potting"; Alizarine black offers great resistance to acids, and is less subject to defects liable to occur in dyeing—especially in after-chroming.[1]

It would almost seem as though, in this case, the potassium chromate does not act as a mordant, since satisfactory fastness to light can be obtained by merely steaming alizarine black that has been dyed in an acid bath. Against these advantages, however, is the drawback that alizarine black easily rubs off wool, thus causing numerous inconveniences in spinning.

Of the newer black mordant dyes, anthracene chrome black, PF, PF ex., PR, PF2B. PFR ex. (Cassella) deserve special mention, being nearest to logwood black in tone and not attended with the defects of the blacks mentioned above. This black is allowed, in the specification of the Prussian military authorities, for dyeing uniform fabrics.

The following black mordant dyes have also been found good in practice: acid aniline black (M.L.Br.), anthracene acid black

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[1] Defects may, however, occur even with this dye, when further batches are dyed in a bath that has been used for after-chroming. This can nevertheless be done in the case of anthracene chrome black and acid alizarine black.

ST, SR, SB, B, etc. (Cassella), salicine black T, WT, D (Kalle), fast chrome black (A.G.F.A.).

On account of its good levelling properties, alizarine blue-black B (Bayer) is largely used as a black in mixed dyes.

Cotton-Dyeing.

Cotton is dyed in the loose condition, as yarn, warps, cops, and in the piece. In the case of this fibre it is a still more difficult task than with wool to give all the various dye-stuffs and combinations used, chiefly by reason of the very large number of direct dyes now so extensively employed for cotton. Consequently, the subject can only be treated in an indicative manner.

In the first place, it should be mentioned that nearly every dyeing on cotton can be performed in three ways—with tannin dyes, with direct dyes, and with mordant dyes. Vat and ice dyes are used for special purposes.

Green.—This class of colours is produced with a basic green dye (brilliant green, malachite green, etc.), either alone or shaded with chrysoidine—or handsomer and faster with auramine. Other shading dyes are also used, such as thioflavine T, the various phosphines, vesuvine, etc. Blues like methylene blue, Nile blue, etc., may be used with auramine to produce green. Of the substantive dyes, thiazole yellow (By.) or thioflavine (C.) may be combined with diamine pure blue (C.) or benzo pure blue (By.), for bright, but fugitive dyeings. Faster bright shades are obtained, *e.g.* by dyeing with diamine pure blue FF and diamine fast yellow, followed by coppering.

Diamine green (C.) has been found very good for medium greens, but must be topped with a basic green dye to brighten up the otherwise very dull appearance of the colour.

A good olive is obtained by dyeing with diamine green, diamine fast yellow and diamineral brown, followed by treatment with chromium fluoride.

The combination: Katigene green (immedial brilliant green) and katigene yellow gives a bright green; and katigene olive a good olive-green.

A fast, bluish-green is obtained with viridanthrene B (B.A.S.F), and a fast olive by olivanthrene (B.A.S.F.). The combination of quercitron with a basic green dye-stuff gives a bright and fairly fast green, which at one time was largely used for piece dyeing.

Different, moderately fast olive-green shades can be obtained, chiefly on loose cotton, by the use of logwood and fustic or quercitron, with or without catechu and basic dyes.

Yellow.—Pure fast yellows are produced on cotton with quercitron and alumina mordants, on piece-goods, but chiefly with chrome yellow in the case of yarns. Less fast, though still fairly so, are the colours produced with various yellow direct dyes, such as chrysamine (which is cheap, but not fast towards alkalis), and the faster chloramine yellow (By.), fast diamine yellow (C.), chrysophenine (By. Act.), diamine golden yellow (C.), Mikado yellow (Leonhardt), etc. Fugitive greenish-yellow tones are furnished by thioflavine, thiazole yellow, etc.; faster shades with auramine. Yellows fast to washing are obtained with katigene yellow (By.), thiogene yellow (M.L.Br.), immedial yellow D, GG (C.); and shades that will stand chloring, with primuline (after-chlored) and flavanthrene G. Brownish-yellow shades, known as chamois, nankeen, etc., were formerly produced with fugitive basic dyes—chrysoidine phosphine—but nowadays better with chrysamine toluene yellow, toluene orange, etc. Iron chamois which is very fast, except to acids, is now very little used. Khaki shades, so popular of late years, are best obtained with sulphur dyes.

Orange.—A perfectly fast orange is produced, chiefly on yarns, with orange chrome, and with alizarine orange on piece-goods. Of the substantive orange dyes, Mikado orange, chloramine orange and toluylene orange may be mentioned on account of their fastness. Of the basic dyes, mention may be made of tannin orange R (C.), and of the sulphur dyes, thio-orange (M.L.Br.) and immedial orange, which give dull shades, fast to washing.

Red.—The fastest red on cotton is the Turkey-red produced by the old process, the so-called "old red". The new red, chiefly produced on yarns and pieces, is also very fast, though not equal to the old red.

Large quantities of cotton are dyed of late years with *p*-nitraniline red (especially piece-goods), the various benzopurpurines, rosanthrenes, benzo fast red, diazo brilliant scarlet and the acid-proof trona red (By.). For many purposes the fairly fast diamine fast red and primuline red (which stands washing) are also used. Finally, red dyeings are frequently obtained with fuchsine or safranine with or without a yellow dye (auramine, chrysoidine, etc.), especially for cotton in mixed wool and cotton fabrics.

Rose-Red.—The handsomest of these colours on cotton is that furnished by rhodamine and a fatty acid salt of alumina or with irisamine G (C.) fixed with tannin; the fastest by alizarine. When alizarine cannot be used, it may be replaced by erica (Act.), brilliant geranine (By.), diamine rose (C.), etc., all of which yield colours that will stand washing. The fastness of these dyeings is improved by the use of rosanthrene, benzo fast red and pink, and thioindigo red.

Bordeaux.—A fast Bordeaux is produced by combining alizarine with methyl violet or rubine, or with alizarine, logwood, quercitron, and alumina-iron mordant, on piece-goods.

Nowadays the following dyes are also used for this purpose: alizarine Bordeaux, thiogene purple, thiogene dark red R, immedial Bordeaux G., various combinations of substantive dyes, such as primuline red and diamine black, primuline developed with Bordeaux developer, diamine Bordeaux, and a combination of safranine, methylene blue and auramine.

Blue.—Vat blue is the fastest and most esteemed blue for cotton. Very important are also the blue sulphur dyes (immedial indoine blue, immedial blue, thiogene blue, thiogene cyanine, melanogene blue, katigene indigo, katigene dark blue, katigene chrome blue (By.), and others). In piece dyeing they are mostly used only for light shades (*e.g.* thione blue) because they oxidise too quickly after dyeing and therefore give uneven colours. Use is also largely made of a number of substantive dyes, such as diaminogene blue, Zambesi pure blue 4B, R, etc. Finally, indanthrene, cyananthrene, and violanthrene (B.A.S.F.), are to be considered for high quality fabrics. Basic dyes, such as cresyl blue, diazine blues, indoine, etc., are seldom used except on piece-goods for discharge effects, or for pure blue dyeings (methylene blue). Finally, mention may also be made of Berlin-blue, which is a fast dye and one still used.

Violet.—A perfectly fast colour is obtainable with alizarine on iron mordant, or with gallocyanine on chrome mordant; the fast alizarine Bordeaux being also used. By itself the alizarine-iron violet is too dull, and must be enlivened by topping with methyl violet. These colours are almost entirely confined to calico-printing and to dyeing in the piece. A brighter, and fairly fast imitation of alizarine violet is obtained by combining safranine with methylene blue, methylene violet, and similar dyes. Very bright and handsome, though fugitive, violet shades are furnished by the various methyl violet marks. Of the direct violet dyes, benzo violet R (By.), diamine violet (C.), etc., are used, and of the sulphur dyes, thiogene heliotrope, thiogene violet B, V, thiogene purple, etc.

Brown.—The most usual method of producing fast browns and drabs, chiefly on loose cottons and yarns, is with catechu, either alone or in conjunction with other dyes. These are often topped with Bismarck brown, to make them brighter. Fast browns on piece-goods are also produced with manganese bistre and by combinations of alizarine, quercitron, and logwood, though more often with sulphur dyes (immedial brown, katigene brown, thiogene brown, etc.). Finally, also, various direct brown dyes, chiefly diamine brown M, diamine bronze, toluylene brown, and benzo chrome brown, are employed.

Grey is still most frequently produced by alternate immersion of the cotton in logwood and iron baths. These dyeings make the fibre hard, and have therefore been largely superseded by sulphur dyes, various marks of diamine black and similar direct dyes. Melanthrene (B.A.S.F.) gives a very good grey.

Black.—This important colour is now mostly produced with aniline black, and to a lesser degree with direct dyes and logwood. The direct sulphur dyes include the different marks of diamine black (C.), oxydiamine black (C.), direct deep black (By.) direct blue-black (By.), Columbia black, etc. Less esteemed are the blacks diazotised and developed on the fibre: diaminogene black (C.), diazo black (By.), Zambesi black (Act.). Of some importance are the after-chromed blacks: various marks of diamond deep black (C.), diamineral black (C.), benzo chrome black (By.), and Columbia chrome black (Act.) (a mixed black), which are fast to rubbing and crabbing (see Finishing), and are used to replace aniline black in dyeing half-woollen goods, the cotton yarn being dyed black, spun with white wool, and the wool topped in an acid bath after crabbing.

Aniline black is still the best black for cotton. Logwood, though of greatly diminished importance, is still preferred to artificial dye-stuffs for some purposes, especially velvets, owing to its richness and bluish tinge. It is, however, only really fast when produced by the aid of copper. The sulphur blacks, the various makes of which are of equal value, play the most important part at present, and are very fast, though not equal to aniline black in this respect. Most of the substantive black dyes will stand washing, but their fastness to light leaves a good deal to be desired, and they have not the same beautiful full appearance as the aniline blacks, with which, however, they still compete, especially certain blacks (*e.g.* diaminogene black) diazotised on the fibre.

Ramie, linen, and hemp are dyed in the same way as cotton; jute is dyed with basic and acid dyes in a weak acid bath, either containing alum (2 to 5 per cent.), or oxalic acid (1 to 2 per cent.). The material is entered at 40° C., heated to boiling, and boiled for a half to three-quarters of an hour.

Dyeing Mixed Fabrics.

The term "mixed fabrics" implies fabrics composed of two or more different classes of fibres. Formerly these fabrics were dyed, in part or altogether, in the form of yarn, but nowadays they are dyed in the piece, by one of two methods, either to one colour, the different fibres being caused to absorb dyes of the same shade, or else "shot" effects are produced by dyeing the different fibres to widely different colours, the result being the more handsome in proportion as the two colours are complementary one of the other.

The suitability of different dye-stuffs for dyeing mixed fabrics can be readily ascertained by dyeing small samples. In this connection it must be borne in mind that not only the nature of the different fibres present, but also their relative proportions in the mixture, is of importance.

Dyeing Half-Woollen Goods (Wool and Cotton).- It is even now occasionally the practice to dye the cotton in the yarn with acid-resisting dyes, then weave it along with white woollen yarn, and dye the wool with acid dyes in the piece. For the most part, however, these goods are piece dyed, there being two methods of effecting this object. The older plan is to dye the wool in the fabric with acid dyes, which, of course, leave the cotton untouched, the latter being afterwards dyed with basic or direct dyes In the first case the goods are treated with tannin on the jigger, fixed with tartar emetic (and iron, if necessary) and finished by treating with a basic dye. In order to preserve the wool as much as possible from alteration, the latter process is carried out in the cold. The final bath may also be lukewarm, but as the wool always absorbs a little of the dye, the shade produced in the first dyeing should be rather lighter than that really required. In the case of two-colour effects the last dye-bath must be cold.

This method therefore entails the use of four baths; and the production of blacks is even more complicated, the cotton having first to be mordanted with iron by treating it with sumach, fixing with iron, and treating with chalk; the wool mordanted next by heating in a bath of potassium bichromate, free from acid (to prevent the iron being extracted from the cotton); and, finally, the whole is dyed with logwood.

A simpler method consists in dyeing the wool first with an acid black, and then the cotton with iron and sumach. A good black is also obtained in half-wool goods by dyeing the cotton with a diazotisable black direct dye (*e.g.* diazo black BHN), diazotising and developing, and then dyeing the wool with an acid black.

If direct dyes be used for finishing the cotton, the fabric should be treated, after dyeing the wool, in a cold or lukewarm bath containing Glauber salt and carbonate of soda in addition to the dye.

Half-wool goods can also be dyed with acid and direct dyes in a single bath, by taking such acid dyes (*e.g.* alkali blue) as are capable of dyeing wool in a neutral or acid bath.

In the second method the half-woollen material is dyed with direct dyes in a bath containing 2 to 4 per cent., by weight, of Glauber salt.[1] This process has the great advantage of simplicity, inasmuch as a black can be dyed in a single bath, *e.g.* with half-wool black (C.), the only difficulty being in dyeing to pattern.

The behaviour of the direct dyes towards wool and cotton is somewhat divergent, some of them enabling the two fibres to be dyed to an equal depth, whilst others dye the cotton only, and are therefore suitable for use in producing two-colour effects. As a rule, the following conditions obtain: in a boiling-hot bath the wool will take up the more dye and come out deeper in colour than the cotton, the converse being the case when a low temperature is used. The addition of a small quantity of an alkali salt, like soda, reduces the absorption of the dye by wool; and, conversely, the wool is dyed more strongly than the cotton when an acid bath is employed.

The *modus operandi* is thus practically revealed. The bath is boiled and steam is shut off, the goods being then entered and worked without heat, until the cotton is of the desired shade. Steam is then turned on and dyeing continued until the colour of the wool appears deep enough. It is generally kept a little lighter than the cotton. The after-darkening or shading of the wool, which is nearly always necessary, is effected with acid dyes, whilst for the cotton direct dyes are used, these drawing better on this fibre than on wool; or the dye may be caused to draw more to the cotton or the wool, as is found necessary, by making the bath liquor alkaline or acid.

If only the cotton in half-wool goods is to be dyed, this is best done with suitable direct dyes in an alkaline bath.

The method of dyeing half-wool goods with direct dyes is of special importance in connection with shoddy, which must first be bleached with hydrosulphite if coloured.

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[1] The calcined salt, though cheaper than the crystals, is not so good for this purpose, since, as a rule, it is not neutral.

The sulphur dyes can also be employed for dyeing half-wool goods, by patented processes (Bayer, Cassella).

Dyeing Half-Silk Goods (Silk and Cotton).—There are two chief methods to be considered in dyeing half-silks—(1) the silk is dyed first, with an acid dye, to a shade rather lighter than actually required, next the cotton is treated with tannin, passed through a bath of tartar emetic, and cold-dyed as quickly as possible with basic dye in a fairly concentrated bath; (2) in this case a first dyeing is given with a direct dye, after which the silk, which is generally too light, is darkened by entering in a bath of basic or acid dye.

This second method has now attained a high degree of practical importance, and will therefore be described in detail.

A study of the behaviour of the various direct dyes towards silk reveals considerable divergences, which, nevertheless, can be classified according to certain laws. In the first place, some of these dyes have the property of dyeing silk and cotton in different tones, and these dyes are the least suitable of any for the purpose now in view. Their affinity towards the two fibres in question depends, in the first place, on their nature, and, secondly, on the constitution of the dye-bath—a greater affinity for cotton being exhibited in a neutral bath containing common salt, or in a weak alkaline bath, whereas in a weak acid bath the dye draws better on the silk. Some of the direct dyes—the reds, for instance—dye cotton and silk almost equally in an alkaline bath, which is charged with 5 per cent. of sodium phosphate, 5 per cent. of soap, and the necessary quantity of dye, the goods being entered lukewarm, then slowly raised to a temperature a little below boiling—not quite on the boil, or the silk would suffer—and, after turning off the steam, continuing to treat in the cooling bath for another half-hour or so.

Many other direct dyes, especially such as dye cotton best in presence of common salt, can be advantageously employed to dye half-silks with common salt and acetic acid, provided the foregoing precautions be borne in mind.

The silk, which is generally rather too light in colour, can be brought up to the proper shade by entering the goods in a fresh bath containing basic dyes and a little acetic acid, at 30°

to 40° C., or with acid dyes at a somewhat higher temperature and with more acetic acid.

For "shot" effects the goods are dyed either by the first-named method, or else first with a dye that attaches itself to the cotton alone, leaving the silk undyed, the latter being afterwards dyed in a fresh bath containing acid dyes.

Black is obtained with either aniline oxidation black or katigene and other sulphur blacks. In the latter case a lactate (Bayer's process) or glucose (Cassella's process) is added to the dye-bath, to protect the silk against the highly alkaline sodium sulphide. If half-silk goods be dyed with sulphur dyes in presence of size, the dye does not touch the silk.

Dyeing Gloria (Wool and Silk) Fabrics.—This method of piece dyeing is of recent date, and is one of the most difficult tasks the dyer is called on to perform, since it entails an accurate knowledge of the behaviour of the dyes towards wool and silk.

Here also, as in the case of half-silks, it may happen that a dye produces a different shade on the wool to that imparted to the silk. Such dyes are therefore unsuitable for the purpose in view.

The acid dyes are those most in use for this purpose, and these, as a rule, dye the wool more strongly than the silk when applied at boiling-heat, the converse being the case at low and medium temperatures.

The following dyes act equally on wool and silk at boiling-heat: Indian yellow G.R., fast green, bluish mark (By.), patent blue, alkali blue, alkali violet, navy blue B (B.A.S.F.), fast blue, greenish tinge (B.A.S.F.), acid violet 6 BN (By.), fast acid violet A2R and 10B (M.L.Br. and By.), Bengal-rose (dyed with acetic acid), anthracite black (C.), naphthylamine black D, 4B, 6B (C.), gloria black, phenol blue-black 3B (By.), etc. The following have a rather stronger affinity for wool: light green S, wool green (B.A.S.F.); the acid orange dyes, like orange II; a few ponceaus like palatine scarlet (B.A.S.F.), brilliant croceine (C.), etc.

On the basis of their affinity for silk and wool, the acid dyes may be divided into three groups, those given above as having an almost identical affinity for both fibres being taken as the first group. To a second group belong such dyes as chiefly dye wool when applied at boiling-heat, *e.g.* acid green, extra conc. (C.), tartrazine, orange G, a few ponceaus, as mark 2R (M.L.Br.), S. pat. (C.), indigocarmine, cyanine (M.L.Br.), azo wool blue C, lanafuchsine SG, 6B (C.), etc. Finally, the third group comprises the dyes having more affinity for silk than for wool at medium and low temperatures—azocarmine (B.A.S.F.), acid violet N (M.L.Br.), fast acid blue B (By.), water blue, etc.; as also the majority of the basic dyes, such as methyl green, auramine, rhodamine, etc.

The best means of dyeing wool and silk to equal shades is by using the dyes of Group I., unless prevented by other reasons such as their equalising properties, suitability for combination, etc. The *modus operandi* is as follows: The bath is set with about 10 per cent. of "tartar preparation," bisulphate, and one-half the necessary quantity of dye, the goods being then entered and the bath raised to boiling-heat as quickly as the equalising properties of the dye permit, boiling being continued until the wool appears sufficiently shaded. The silk will, as a rule, be less deep in colour; consequently, after cooling the bath down to 45° to 50° C., the rest of the dye is added, and the operation continued in the cooling bath until the silk has been properly dyed. If, however, this result fails to ensue, recourse must be had to a suitable dye of the third group. In this manner a light yellow may be obtained with azoflavine, which, however, turns dirty in dark shades; a dark yellow and orange, with orange II; red, with azocarmine, magdala red, or a ponceau; pale blue, with patent blue; dark blue, with acid violet 6BN and bluish fast green; black, with anthracite black (deepened with orange and a basic green at low temperature), gloria black, etc. For mode colours, use is preferably made of azocarmine, patent blue, and azoflavine.

To produce "shot" effects, the following procedure is adopted: The wool is dyed first with a dye of the second group, at boiling-heat; the small amount of dye that has become fixed on the fibre of the silk is then removed by boiling with water, soap, or ammonium acetate, and the silk afterwards dyed in a third bath, containing a dye of the third group, the bath being concentrated and cold, or, at most, lukewarm. Red, for instance, is produced on the wool by the aid of ponceau 2R, and the silk dyed green with methyl green and auramine; or the wool dyed green with acid green extra conc., the silk red with rhodamine, etc.

The most beautiful effects can be produced in this way, but the following points must be borne in mind: (1) The dyeings on the two fibres must be as nearly equal in intensity as possible, and complementary; (2) the silk must be thoroughly freed from colour after the first dyeing; (3) the dyes employed in the third bath must have a low affinity for wool. These conditions, however, are rather difficult to carry out in practice, and, moreover, the three baths render the operation very troublesome; consequently, the general procedure is to first dye the wool with dyes of the second group, then cool the bath as much as possible, and dye the silk with dyes of the third class.

An important mixed effect is: wool black, silk white. This can be produced in various ways: by dyeing with a suitable acid black (chrome acid black, etc.); or by dyeing with azofuchsine at boiling temperature in a strongly (acetic) acid bath, and then treating with bichromate of potash. The silk is cleaned in a bran bath.

Finally, it may be mentioned that fabrics of three different fibres (wool, silk, and cotton), such as damasks, are frequently piece dyed, the same procedure being adopted as given above for dyeing half-wool and gloria fabrics.

V. Sample Dyeings; Colorimetric Determinations; Reactions of Dye-Stuffs on the Fibre; Tests for Fastness.

Sample Dyeings and Colorimetric Determinations.

The determination of the value of dyes is made by sample dyeings or by means of the colorimeter, though in either case all that can be done is to effect a comparison between two or more samples of one and the same dye, or two or more very similar dyes. In both cases it must be borne in mind that minute differences in the intensity of two dyeings can only be detected in light shades. The greatest difficulty is encountered in examining yellows, and therefore in this case it is advisable to combine the dye in question with another dye of suitable character, *e.g.* a blue.

Sample Dyeing consists in making comparative dyeings with two or more parcels or samples of one and the same dye under closely identical conditions, and examining the resulting colours for their relative intensity, shade, and purity.

In the dye-stuff factories this work is essential, to enable a new dye-stuff to be standardised in point of strength, this being the only possible way of turning out a given commercial article of constantly uniform quality.

In dyeworks, too, each new parcel of dye-stuff should be tested in the same way, to ascertain whether it is identical with previous deliveries.

With this object a small quantity, say 1 grm., of each sample of dye is carefully weighed out and dissolved in 1 litre of water, each solution being then employed to dye equal weights of yarn in baths of otherwise identical constitution, and all under the same conditions of temperature. The best method of applying heat is to immerse the dye-baths in a heated strong brine. When mordant dyes are in question, the various samples of yarn must be mordanted beforehand in one and the same bath. Already during the process of dyeing it will be easily seen whether any considerable differences exist between the various samples, and should this be the case the weaker bath must be strengthened by adding sufficient of the dye solution to bring the dyeings into a condition of equality.

Many direct sulphur dyes are very irregular in point of strength, as sent out by the makers, and it is in part very difficult to make sample dyeings with these.

It will also become apparent during the dyeing whether the dyes are homogeneous or mixtures, since the different dyes never draw on to the fibre so uniformly and simultaneously as to render the detection of a mixture impossible.

After dyeing, the samples are washed, dried, and the resulting difference determined with reference to the amount of dye consumed. At the same time it will have to be ascertained whether, through unequal heating, the one bath has become

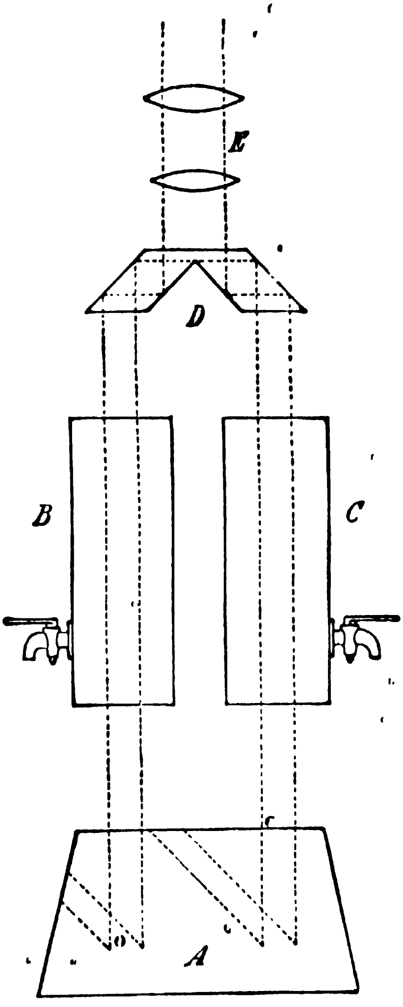

Fig. 35.

more highly concentrated than the other. Should this prove to be the case, the test must be repeated, since more dye is taken up from concentrated baths than from those more dilute. If the baths have been imperfectly exhausted, another dyeing with fresh yarn will give an idea of the quantity of dye left behind the first time.

A simpler, quicker, and more accurate method is afforded by the colorimeter, though this is more suitable for the scientific examination of dye-stuffs than for determining their technical value, the results it gives being influenced by impurities which may be quite inert so far as the dyeing process is concerned. Of the various types of this instrument, mention need only be made here to that of C. H. Wolff, the construction of which is based on the fact that light rays suffer a diminution in brightness in passing through a stratum of coloured liquid, the decrease being in proportion to the degree of concentration of the liquid, *i.e.* the greater the quantity of dye in the liquid, the more will the light be dimmed in passing therethrough.

The accompanying sketch (Fig. 35) will facilitate description of the Wolff colorimeter :—

B and *C* are cubed cylinders into which the dye solutions are poured; *A* is a reflector; *D* a pair of prisms, which so unite the two bundles of light rays in the field of vision of the lens *E* that the one half of the circular field of vision corresponds to the light transmitted through the one prism, and the other half to the rays traversing the other prism.

The two solutions for comparison, which must be very dilute, are placed in the respective cylinders and examined, the darker one being reduced in volume by drawing it off through the lateral tap until both sides of the field of vision appear of equal intensity of colour.

Now the capacity of absorption for light is inversely proportional to the thickness of the absorbent layer traversed by the rays. Thus, for example, if to produce equal intensity in the two halves of the field it is necessary to reduce the one liquid to half the volume of the other liquid, then the absorptive capacity of the former will be double that of the latter. As, now, the absorptive capacity of a liquid for light depends directly on the degree of concentration, then, by assuming the height of the two columns of liquid in the test cylinders as being represented by *H H′*, whilst the concentration of the liquids is expressed by *C C′*, we obtain the following simple relation :—

$$C : C' = H' : H.$$

The relative colour strength of the solutions under examination can be easily calculated by the aid of this proportion.

In making a determination it is not advisable to confine the examination to a single test, but to make at least two, which should differ by not more than about 2 c.c.

Good results with the colorimeter can only be obtained when the shade of colour of the dye solutions to be compared is the same in both, and the solutions are very greatly diluted. To ascertain whether a given concentration is suitable the two solutions in the colorimeter are diluted until of equal depth of colour. If the adjustment is right (*i.e.* the proper concentration has been chosen), the drawing-off of 1 to 3 c.c. of the one solution will cause the field of vision to appear lighter at once. If this is not apparent, the solutions in question are either too strong or too dilute.

Reactions of Dye-Stuffs on the Fibre.

In practice it is frequently desirable to ascertain what dye has been employed to produce a given dyeing, and with this object the sample is cut into strips which are then subjected to the action of various reagents, such as acids, alkalis, alcohol, etc., in order that some conclusion as to the nature of the dye can be drawn from the colour-changes ensuing therefrom. Owing to the large number of existing dyes this method is by no means easy, and, especially in the case of mixtures, is often only partially possible. For the assistance of the dyer, various tables, setting forth the necessary indications, have been compiled.

In view, however, of the extremely large number of the dye-stuffs used, working with the aid of these tables is difficult and uncertain. On the other hand, a very reliable new method has been established by Professor A. G. Green, for application to dyeings on wool and on silk.

Green's Table for Testing Wool and Silk Dyeings.

Behaviour towards Hydrosulphite.

The sample is boiled with a 10 per cent. solution of hydrosulphite NF. In the case of yellow and orange dyeings 200 c.c. of the hydrosulphite solution are acidified with 1 c.c. of acetic acid.

1. The solution is decolorised:—

(*a*) The colour returns after exposure to air: Azines, thiazines, oxazines, indigo, prussian blue;

(*b*) The colour is not restored by exposure to the air, but when warmed with a little water and treated with a cold saturated solution of persulphate carefully added, drop by drop: triphenylmethane group, insoluble red-wood dyes;

(*c*) The colour returns on exposure to air, but more quickly, or being treated with persulphate: stilbene group (not all);

(*d*) The original colour is not restored by exposure to air or by treatment with persulphate: azo dyes, nitro- and nitroso-dye-stuffs. In the case of safranine azo dyes (indoine-blue, Janus blue and green, diazine green), a reddish colour is produced after exposure to air (formation of formaldehyde).

2. Not decolorised, but changed into yellow to brown: alizarine, alizarine orange, alizarine blue, cæruleine, naphthazarine, alizarinecyanine green, alizarine viridine. The colour is restored by exposure to light in the case of alizarine blue, cæruleine, and naphthazarine, and by treatment with persulphate in the case of others: alizarinecyanine green and alizarine viridine.

3. Only slight change if any: Pyrone group, auramine, quinoline and acridine dye-stuffs, thiazole dyes (except azo dyes), a few oxyketone dye-stuffs, such as flavone, alizarine yellow, catechu, alizarinecyanine; alizarinecyanine black, anthragallol, aniline black.

If, by means of this table it is considered that a dye-stuff has been identified on the fibre, a trial dyeing is made with such dye on a fabric of the same kind as that under test, and is tested with the same reagents, in order to ascertain the identity or otherwise of this dyeing with the one under examination.

An excellent method for the reliable identification of dye-stuffs is that of spectrum analysis elaborated by J. Formánek; but, like the colorimeter, it requires some skill and a good eye.

When the identification of a sample of dye-stuff is in question, the method of Gulinow ("Zeitschrift für Farbenindustrie," 1906, Part 18) is used.

Boil 1-2 minutes with 5 per cent. Acetic Acid.

Much of the dye is extracted.
BASIC AND NATURAL DYES.
Boil 1-2 minutes with dilute alcohol (1 : 1).

No colour is extracted. Natural Dye-stuffs.

Much of the colour is extracted.
BASIC DYES.
Boil with hydrosulphite to identify the basic dye. To differentiate the yellow dyestuffs which are not decolorised by hydrosulphite:

Treat the fibre with concentrated sulphuric acid:

1. Green fluorescence of the solution: *Acridine Dyes;*

2. Fibre completely decolorised: *Auramine;*

3. Fibre and solution dull yellow: *Thioflavine.*

Little or no extraction of dye:
ACID DYE-STUFFS, DIRECT DYES, MORDANT DYES.
Boil 1-2 minutes with ammonia (1 part concentrated NH_3 + 100 parts H_2O) and test with a small piece of white cotton:
(For Bordeaux, violet and black: 1 part concentrated NH_3 + 50 water and 50 alcohol.)

Much colour comes down, but the cotton remains undyed:
ACID DYES.
Boil with Hydrosulphite.

Little or no change.
Red dyeings: acidify the ammoniacal extract:
1. Precipitate formed, fluorescence disappears. *Eosines.*
2. No precipitate, fluorescence retained. *Acid Eosines.*

Decolorised.
Yellow dyeings:—
Treat the ammoniacal extract with concentrated HCl:
1. Unchanged: Tartrazine, Orange G., 2 G.R., etc.
2. Decolorised: Naphthol yellow, Martius yellow.
3. Turns red: Fast yellow, Indian yellow and similar dyes.
4. Turns red or violet: Metanile yellow, Orange IV.

Red dyeings:—
Boil with dilute bichromate:
1. Colour changes to blue: Azofuchsines, chromotrope etc.
2. No change: evaporate the ammoniacal extract and dissolve the residue in concentrated H_2SO_4:
Red: Xylidine and Palatine scarlets.
Violet: Crystal ponceau, fast red A, etc.
Blue: Croceine scarlet, fast red B, etc.
Green: Biebrich scarlet.

Little or no colour deposited:
The cotton remains white: *Mordant Dyes;*
,, ,, is coloured: *Direct Dyes* (many black direct dyes, however, do not come down and therefore do not dye the cotton).

(If a red dyeing is turned violet by ammonia, cochineal or cudbear is indicated. The former is turned to dark yellow by hydrosulphite, and the original colour does not return on exposure to air. Cudbear is decolorised but the colour comes back in the air.)

Treat for 2-3 minutes with a 5 per cent. solution of sodium acetate in presence of a small piece of white cotton.

The Cotton is

dyed:
Direct Dyes and Azo-mordant Dyes (chromotrope, anthracene black and red, etc.).
Test for Chrome Mordant:
Reds: test with concentrated H_2SO_4; other colours: boil with hydrosulphite.

left undyed:
Mordant Dyes, Indigo.
Test ash for mordant:
Blues: Boil with a little aniline: blue solution obtained, which on being heated after evaporation, gives off violet fumes; *Indigo.*
Blacks: Boil with dilute HCl (1 : 10):
1. Fibre blue, solution red: Black with indigo bottoming and logwood.
2. Fibre and solution red to light brown: logwood.
3. No change: Test further with hydrosulphite, this applying also to colours other than blacks.

Testing the Fastness of Dyes.

Fastness in dyes is a quality of equal importance with cost and colour, and a dye can only be considered as really fast when it proves capable of resisting for a sufficiently long time, without appreciable alteration, the influences to which it will be subjected in practical use.

It is not essential that a dye should be fast in every respect. For example, in the case of clothing, all that is required of a dye is that it will stand the various influences to which it will be exposed in wear; in the case of curtains, fastness to light is a prime essential; whilst the dye on underclothing, worn next the skin, must be able to withstand friction and perspiration.

Tests for fastness, however, never furnish more than relative values, and consequently these tests are best made by comparison between at least two dyes, or their dyeings, simultaneously—a necessary condition being that the dyeings in question shall be of as nearly equal intensity as possible.

Fastness to Light implies the power of a dye to withstand the combined influence of light and air. The chemical reaction that goes on during the fading of a colour has not been minutely examined, all that is known being that, in the absence of air, the influence of light is considerably reduced.

The fastness to light of any given dye depends on several circumstances, *e.g.* on the nature of the fibre, the method of fixing, and the intensity of the dyeing. Thus, dyeings on wool are mostly faster to light than those of the same dyes on other fibres, whilst in the case of logwood dyeings, the colour is faster when consisting of an iron or copper lake, the alumina and tin lakes being fugitive. The basic dyes are generally much faster to light when fixed with tannin or tartar emetic than with oleic acid, on cotton. Finally, as regards the effect of intensity on the fastness to light, it is evident that a dark shade containing a larger quantity of dye will be able to stand the influence of light a far longer time than a light dyeing, not to mention that under the latter circumstances a slight change—especially of a qualitative nature—is more readily detected than in dark shades. Thus when, for example, a blue dye has the tendency to become greener in the light, this faculty may pass entirely unobserved in the case of dark shades, whereas in light shades it may result in a complete modification of the colour.

The manner in which a colour suffers alteration is therefore an important point; when it merely becomes paler, without losing its brightness and tint, it is decidedly faster to light than one that suffers a change of tone in the same time.

In exposing dyeings to light, two other peculiarities become apparent: some dyes (*e.g.* indigo) rapidly becoming lighter at first and then remain for a long time without further change; others again (*e.g.* picric acid, azoyellow, etc.) turn somewhat darker at first.

Two forms of apparatus have been constructed for testing the fastness of dyes to light, that used by Oehler being arranged so that a collecting lens directs the concentrated rays of the sun in a vertical direction on to the material. The other apparatus, that of H. Perger, is illuminated by the electric light. In applying the test it has to be remembered that the intensity of the action exerted by the light depends on several circumstances —the time of year, climate, weather, and, finally, the manner in which the exposure is made; consequently, the tests in all cases must be comparative, and made with at least two dyeings at the same time. When the fastness of a dye is known, this can be taken as a standard and used for comparing that of another exposed under the same conditions. The dyed samples are laid out flat on a sheet of strong paper, the one half of the sample being exposed, whilst the other half is covered over by a piece of cardboard, and, being thus protected from light and air, serves for comparison. The samples are then exposed freely (not under glass) to the sunlight in a place where they are protected against dust and also against acid or alkaline fumes. The use of other sources of light, such as the electric light, gives different results, and therefore is not suitable for practical purposes. At the start the illuminated and protected portions of the sample should be compared daily, and an incipient change in the colour must not lead to the abandonment of the test, it being further necessary to examine the progress of such change. Dyes that will stand exposure for a month in the summer without appreciable alteration may be considered as very fast to light.

Fastness to Water, Washing, and Milling, implies the behaviour of dyes under the action of water or solutions of soap; and the points to ascertain are whether the dye changes in colour or intensity, and if it bleeds into white or undyed fibre with which it is washed. The requirements exacted in this particular vary considerably, carpets, curtains, and upholstery stuffs, for instance, not being required to stand washing, as a rule; whereas yarns that are to be woven into pattern fabrics and then milled must remain entirely unchanged during that operation and exhibit no sign of bleeding.

In testing a dye for its fastness to water, a sample of yarn dyed with the specimen under examination is plaited along with a piece of white yarn and left immersed in cold water all night. To be quite fast, the dye must not dissolve in the water, and thus colour it, or bleed into the white yarn. In the case of woollen yarns this test is usually performed by boiling the sample in water for a quarter to half an hour.

Fastness to Washing and Soap is tested by plaiting a sample of dyed yarn with white yarn and then treating them for a quarter to half an hour in a solution of soap (about 0·2 per cent.), first at 50° to 60° C. and then at 100° C.

Fastness to Milling is required of woollen goods only, and is tested by subjecting the plait of white and dyed yarn to a rigorous milling by hand, with an alkaline soap, then washing and leaving to stand overnight in a rather wet condition. For the dye to be really fast, it is necessary that no staining of the white should occur, and also that the dyed sample remains free from alteration. The test will be still more severe if the sample be left for several hours in the soapy solution after milling.

In testing wool-dyeings for **Fastness to Acids,** the sample is carbonised with sulphuric acid and then neutralised. Cotton-dyeings are regarded as fast to acid when they will stand dyeing in an acid bath, as applied to wool, without suffering any appreciable alteration of shade or bleeding into white wool. With this object the dyed cotton is boiled along with white wool in a bath containing 4 per cent. of sulphuric acid and

10 per cent. of Glauber salt (calculated on the weight of the wool) for an hour. This test serves to determine whether a given dye is suitable for use on cotton that is to be woven along with animal fibre which is afterwards to be dyed in an acid bath in the piece.

Fastness to Perspiration.—There is, unfortunately, no satisfactory test for this quality, but the general practice is to immerse the sample for an hour, in association with white cotton and wool, in a 2½° B. solution of acetic acid at 40° C. According to Davidis it would be more correct to use an alkaline solution for the test, leaving the sample for ten minutes in a solution of 5 grms. of Marseilles soap and 3 c.c. of ammonia per litre, at 50° C., then squeezing and ironing between white cloths.

Fastness to Bleach (chemicking) is tested only in the case of cotton, the dyed sample being steeped for an hour in a cold 1° B. solution of bleaching powder.

Fastness to Sulphur is a test applied solely to wool. The sample, plaited along with white yarn, is first soaped, squeezed, and then left for twelve hours in an atmosphere of sulphurous acid.

Fastness to Alkali is tested in various ways but mention will now be confined to the quick-lime test often applied in the case of wool-dyeings, the stuff being padded over with a pulp of slaked lime, left to dry, and examined for alteration after brushing off the lime. This test, as well as sprinkling the stuff with soda solution, followed by drying, is performed when information is desired as to the capacity of the dye for standing the influence of street mud.

Fastness to Ironing and Steaming is tested by subjecting the dyed sample to hot ironing or drying on a surface of heated metal, and by steaming. The dye should either be quite free from alteration or else resume its original shade after a short exposure to the air. In applying these tests it must not be forgotten that the wool itself may assume a yellowish tinge under excessive steaming, the result being an apparent alteration of some colours—blue, for example. For the sake of comparison, it is therefore necessary to steam an undyed sample of the same material at the same time.

CHAPTER V.

PRINTING.[1]

WHEREAS the object in dyeing is to secure uniform and complete coloration of the entire material of the fabric, the purpose of the printer is to apply the colouring matters only in certain parts and in a well-defined pattern; hence, printing may be regarded as local dyeing. Closely allied, however, as these two branches of the subject may be, it follows from the nature of the case that the ways and means whereby their respective objects are secured must be very different. For instance, in dyeing, it is for the most part feasible to modify a dyed colour by the subsequent application of other dyes; but in printing this is not possible, and therefore all the materials employed must be carefully examined before use.

For the application of dye to certain parts of a fabric, and according to a well-defined pattern, recourse must be had to an application unknown in the dyeing process, namely, a printing block or forme, by means of which it becomes feasible to print any dissolved dye upon the fabric. It is, however, evident that although the dissolved dye may be printed as a well-defined pattern on the fabric, the contour of the design would very soon lose its sharpness of outline, owing to the running of the solution; and to prevent such an occurrence a further adjunct, rarely if ever used in dyeing, has to be called in aid, namely, an agglutinant, or thickening material, with which the colour is incorporated before application. Apart from this, the colour has to receive other additions, and also to be subjected to certain after-treatments, which will be dealt with later on.

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[1] The author is indebted for much of the information contained in this chapter to the handbooks on Calico-Printing by Lauber and Sansone, and the article on Printing by Storke and Benade, in Karmarsch-Heerens' Technical Dictionary, to which sources the reader is referred for points of detail, especially as regards the compounding of the printing materials.

Besides direct printing, there are other means whereby a coloured pattern can be produced in cloth-printing. Thus, if a fabric be printed over with substances that are impervious to liquids, and is then dyed, it follows that the dye will be fixed only on the unprinted parts of the fabric, the printed portions being left white when the goods have been washed. This kind of printing, whereby white figures can be produced on a coloured ground, is known as "reserve printing" and the substances employed to protect the printed portions from the action of the dye are called "reserves".

Again, it is possible to produce white figures on a dyed material by printing it over with substances that destroy or discharge the colour. This is the so-called "discharge printing".

By the assistance of reserve and discharge printing it is possible to produce patterns in two ways: either a mordant is added to the reserve or discharge before printing, and the goods afterwards dyed, whereby the discharged or reserve portions become coloured because of the mordant there situated; or the reserve or discharge is incorporated with a dye, and then printed. Finally, as a third method, the fabric may be printed with a mordant, which is then fixed in a suitable manner, and the goods dyed, whereupon only the mordanted portions will retain the dye, leaving the rest white, the method being thus a combination of printing and dyeing.

Historical.—From the very earliest times the peoples of the Orient have practised the art of cloth-printing; and although the work was performed in a highly-primitive manner, the above-mentioned methods of producing coloured patterns would seem to have been known to them.

The most primitive state of transition between dyeing and printing is found among the Chinese, who are known to produce coloured figures on cloth by hand-painting.

The true home of the cloth-printing industry, however, seems to be India, printing blocks for the production of coloured designs having been in use there-from the most ancient times. Reserve printing must also be classed as an Indian invention. In the Bandhana method, which is the oldest resist process, knots were tied in the cloth, which were then dyed; whilst in the Golgas method the fabric is pressed between metal stencil plates and entered into a dye solution. In both cases the dye is kept away from certain portions of the fabric by the aid of pressure.

In printing the so-called "Battick" goods that are still produced in Sumatra and Java, the design is drawn on the goods by the aid of a mixture of resin and wax, which are applied in a melted state, and, after solidification, form an impenetrable reserve, so that the parts thus covered remain undyed when the fabric is afterwards dyed (usually by vatting). On subsequently removing the reserve by hot water, there appears a white design on a coloured ground.

This method was first brought into Europe by the French, from their colonies in Eastern Asia, as the so-called "porcelain-printing" (white on blue ground).

The first calico-printing factory on record was established at Richmond-on-Thames in 1676 by a French refugee; later on, works were started at Neuchâtel (1689); in several German towns—Augsburg, Heidenheim-on-Brenz; at Sainte Suzanne, in France; in Austria (Bürgstein, Schwechat, Friedau, Kettenhof, Kosmanos), etc.

At first hand-presses were employed, the design being deeply engraved on a copper plate, which the printer covered with colour by the aid of a brush, the excess being afterwards removed with a knife. When thus ready for printing, the plate was raised by the mechanism of the press, brought into contact with the material to receive the impression, and then returned to the first position, for re-inking.

This method is cheap, and gives a sharp impression. It is still employed—in Switzerland, for example—generally for broad designs, and chiefly for silk kerchiefs.

At a later period other machines were introduced, the most important being the Perrotine (invented by Perrot of Rouen, in 1834), which can also be used as a multiple-colour machine.

The "Hexe" press is still to be found in a few cloth-printing works. At present, however, the cylinder printing-press, first introduced by Bell in 1785, is the most widely used of any.

The early printing colours were prepared by stirring pigments in oil. The effects were very imperfect, the colour flowing at the edges of the design and the fabric becoming hard. Later on, the "application method" was introduced, in which the mixture of mordant dye-stuffs and mordant was printed on a platen and fixed by hanging the fabric in a warm stove. Finally, steaming was employed, towards the end of the eighteenth century, for developing and fixing the printing colours.

Hand-Printing.

The printing plates used must not be too large or too small, the former defect meaning excessive weight and trouble in handling, whilst in the other extreme the work takes too much time.

The material for the plates must be durable and not easily warped, choice being therefore made of pear-, beech-, and box-wood, thin (about one inch) boards of which are glued on the back of similar boards of oak or beech, which in turn are backed by blocks of pine, the latter being recessed so as to hold better. The boards must be arranged so that the grain runs in different directions, in order to minimise the tendency to warp. The under (free) side of the first piece of wood is planed smooth.

To transmit the pattern to the block, the designer divides the pattern by horizontal and vertical lines, so as to include within the marked-off portion all the elements of the pattern, these lines being then transferred to the chalked block. The design is next traced with pencil and paper, the tracing being then laid face downwards on the marked block, and the reverse is rubbed over with a hard, smooth tool, the impression being afterwards touched up by hand. As each block can only be used to print one colour at a time, a separate block must be used for each differently coloured portion of the design.

The tracing of the pattern is never so large as the block, and must therefore be transferred as many times as are necessary to cover the surface of the block. Where the repetition of a small pattern is in question, a small model is often made, the impression being repeated on the block until the entire surface is covered. To ensure accuracy of position, use is made of register pins, which are placed on both sides of the printing block, and in applying the latter, care must be taken to see that the pins on the left side exactly coincide with the marks left by those on the right-hand side during the previous impression. In succeeding rows, the upper pins must register with the marks left by the lower pins.

The design thus transmitted must be brought into relief by punching the wood with steel punches. Where the printing surfaces are large, it is a frequent practice to merely punch the outlines and fill the intermediate space with felt, which substance absorbs the colour much more uniformly than wood and therefore prints better.

Fine-details cut on wood are liable to rapid wear, and are therefore generally done on copper or brass inlaid in the wood block. Frequently, however, the entire surface of the printing forme is of metal, the design being imparted by casting. For this purpose a perfectly dry block of lime-wood, cut crossways of the grain, is taken, and punched with the design, which in this case is hollowed out, the lighter details being burned out by means of heated steel dyes pressed against the wood until the impression has reached a certain depth. The contours of the larger and heavier parts of the design are cut. This done, the hollows are filled with pieces of brass so that the metal projects a few millimetres above the surface of the block, and a molten alloy of tin, lead, and antimony is then applied, which envelops the brass and transmits sufficient heat to the depressions in the wood to carbonise the surface, which is thereby smoothed and deprived of the tendency to shrink. Thereupon the brass is removed, and the resulting wooden matrix or mould is used for making the cast. The casting is trimmed smooth with the file and nailed on to a wooden backing.

Other appliances required for printing with the hand-press are a frame and ink-duct, the former consisting of a strong framework supporting a planed block of hardwood, the dimensions of which vary according to the class of work to be done—a narrow block being needed for long fabrics, and a wide one for kerchiefs. This block is covered with a tightly stretched layer of flannel (printer's blanket), serving as a soft backing for the goods.

On one of the narrow ends of the frame is an arrangement supporting the roller from which the goods to be printed are unwound. The goods issuing from the press are carried over guide rollers, either on the ceiling of the printed room or underneath the frame, for the purpose of drying the printed colour.

The ink-duct is a rectangular trough, about twenty inches long and wide, and ten inches deep, which is filled about half-full of starch paste, for the purpose of forming an elastic bed, upon which is laid a piece of oilcloth stretched on a frame into which fits a second frame carrying a stretched cloth, the colour being spread out on this last, by the aid of a brush, as evenly as possible.

To begin printing, the end of the cloth is laid on the press table and marked with a ruler and pencil, to show where the block is to be applied the first time. The block is then brought into contact two or three times with the inking-pad, and then applied to the cloth, a few blows with the mallet forcing the colour into the material; which done, the block is removed, re-inked, and applied again. In this second and all succeeding applications the block must be made to register by means of the aforesaid register pins, which should be situated in such a position that their impression, though visible to the printer, forms part of the coloured design.

In multiple-colour printing, the work is begun with the block giving the most comprehensive idea of the whole design.

In printing "squares," the fabric is first divided by lines indicating the limits of each square. The blocks for this work are mostly arranged to print one quarter of the whole square.

Some colours must be printed warm, for which purpose the inking-pad must be set on hot bricks or immersed in hot water. When readily oxidisable colours are used, they should be stored in the lower part of the inking-pad instead of the starch paste, and be covered over with a porous cloth.

Unless the cloth be kept on the stretch whilst on the press table, it will shrink, both in length and breadth, in the drying, and thus prevent the last-applied colour registering with the previous ones. To obviate this difficulty the colours must be applied in succession as quickly as possible, or else the fabric is stretched in both directions after printing each colour.

Full shades cannot be printed on thick fabrics by the hand-press. The method is specially suitable for the production of multiple-colour printings and for very wide goods, since to employ mechanical presses for these classes of work would necessitate the use of very complex or wide, and in either event very costly, machines. Hand-printing is also superior to the machine-press, inasmuch as it does not dirty the white.

The Perrotine Press.

The Perrotine press is a machine for printing from cast-metal plates carrying the design in relief, and resembles the hand-press in its points of superiority over the cylinder press. The number of colours, however, that can be printed in this press is limited, and it is now used to only a very small extent. A three-colour Perrotine press is shown, as a diagrammatic sketch, in Fig. 36.

Here *a* is the backing cloth, forming an elastic support for the goods ; *b* is a piece of unfinished cotton cloth, to keep the backing cloth from being dirtied by the printing colour ; *c* is the cloth to be printed ; h_1, h_2, h_3 are the printing tables, furnishing the solid backing. The slides n_1, n_2, n_3, which move in the direction of the arrows, and carry the block-holders o_1, o_2, o_3, press the blocks p_1, p_2, p_3 alternately against the inking-pads q_1, q_2, q_3, which themselves have a reciprocating motion at right angles to that of the blocks. At the moment the blocks are withdrawn from contact with the printed surface, the pads are moved so as to pass by the pairs of rollers r_1, r_2, r_3, which in their rotary motion take up the colour from the ducts s_1, s_2, s_3, and pass it on to the pads, where it is smoothed level by the brushes t_1, t_2, t_3. The slides next advance and press the blocks against the pads, then retreat, and after the pads have been moved slightly to one side, again press the blocks on the pads. The impression then follows immediately, during which operation the pads are moved over the inking rollers. After each impression the backing cloth, intermediate cloth, and cloth to be printed are moved forward a distance corresponding to the exact breadth of the block, so that the goods are fully printed by the time they pass away from the third block. If desired, the advance of the goods can be stayed, and the movement of the printing mechanism continued, the im-

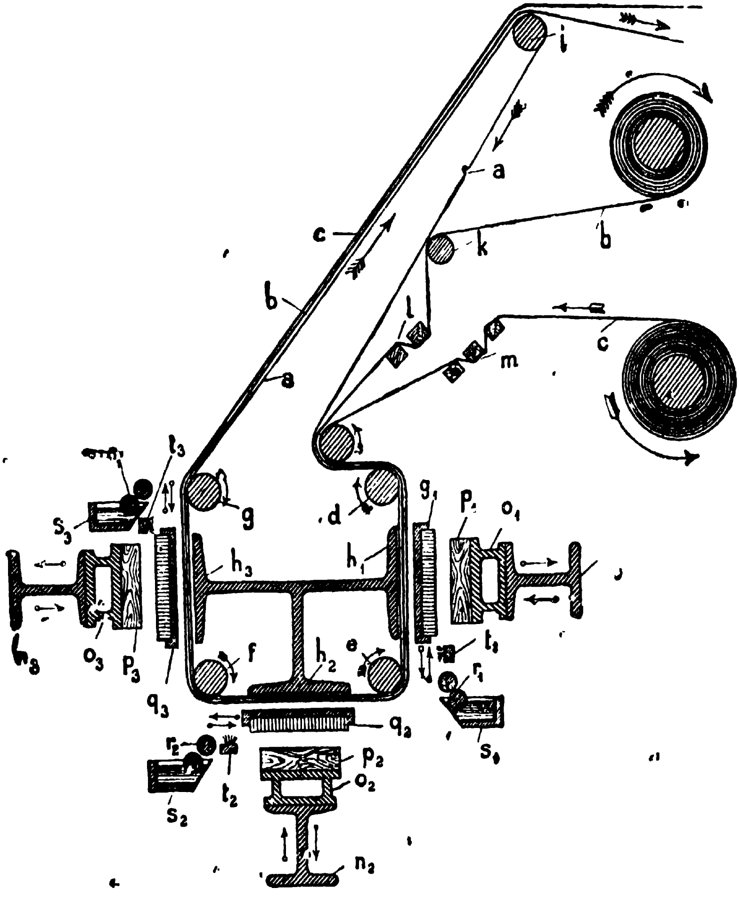

FIG. 36.

pressions being in such case repeated in exactly the same place as often as required.

The Cylinder Press.

In the cylinder machine the impression is produced by means of engraved rollers, known as copper rollers, though they really consist of an alloy resembling bronze. They are in the form of a hollow cylinder, into which are forced a wedge and a steel spindle carrying a pinion by means of which the cylinder is set in motion.

In this case, therefore, it is necessary for the goods to be pressed into the depressions of the cylinder, in order to take up the colour; hence a heavier pressure is needed than in the case of the hand-press, and the machine must be driven by power—a condition lying at the root of the high productivity of the cylinder press, and one that renders it the sole class of machine suitable for the production of printed goods on a large scale. This press exhibits the further advantages of giving a sharp impression and perfect register in the case of multiple colour patterns.

The cylinder press may be of either the single-colour or the multiple-colour type, and each press is driven by its own motor.

A single-colour machine will print up to 180 pieces of 60 to 70 yards each per diem of ten hours. With multiple-colour machines the working speed is much slower, a twelve-colour machine, for instance, only printing about forty pieces a day.

Engraving the Printing Cylinders. As already mentioned, the design is engraved on the cylinders. In order to hold the colour better on broad parts of the design, the surface is there hatched with V-shaped channels, or punched with conical stipples.

The engraving of the design is effected in various ways. The method apparently at first sight most suitable—namely, to trace the design on the surface, and then cut it out with the graver—is really the one least in use, and then only employed for the outlines when the portions of the design to be engraved are so large that they do not repeat, or only partly so.

In all other cases, *i.e.* when frequent repetitions of the same figures occur, a small steel roller is prepared, by means of which the pattern is pressed into the surface of the cylinder, the roller being in relief.

The engraving of the cylinder is frequently effected by etching, either alone or in conjunction with the foregoing method. For this purpose the cylinder is coated over with asphalt lacquer, the lines of the pattern being then drawn in the asphalt so as to expose the underlying metal, after which the cylinder is immersed in dilute nitric acid, which etches out the exposed parts and leaves the design engraved on the metal.

The sole decisive factor in the choice of methods is speed. Most frequently the work is done by the aid of a steel roller or "molette," on which the design is formed in relief by the following indirect process, the direct method being too difficult to attempt. For this purpose a steel cylinder of very good quality and suitable length is exposed to red heat for about twelve hours, embedded in a mixture of powdered charcoal and chalk, and placed in an iron box surrounded with loam. It is then covered with ashes and left to cool very slowly for two to three days, whereby the steel becomes soft, and is afterwards turned and polished to the exact size required, *i.e.* until its peripheral measurement is equal to the width of the pattern. The next step is to clean it by scrubbing with lye, levigated chalk, and dissolved soap, followed by a short immersion in a dilute solution of copper sulphate, rinsing, and drying. To transfer the design to this cylinder, a tracing of so much of the pattern as will be printed of the one colour is made upon satin paper, rendered transparent by impregnation with a solution of gum dammar in turpentine, the tracing ink employed containing sodium sulphide. This tracing is wound on the cylinder, fastened thereon, and left for a quarter to half an hour, by which time the design will be developed by the formation of copper sulphide on the surface of the cylinder. The lines thus marked are cut with a steel graving tool shaped like a slightly bent prism of rhombic section and ground off aslant at the end, thus leaving the convex edge of the prism to terminate in a projecting point. After the outlines have been cut out the conical stipples are punched to a certain depth in a machine, then deepened by hand with a hammer and punch, and finally bored out. They must be set at equal distances apart, and in rows of uniform direction. The hatching is effected with double cutter gravers, the one cutting edge working in the groove already formed, whereby perfect regularity in the position of the hatched lines is secured. Mostly, however, the hatching is produced by etching, the lines being drawn on the asphalted surface by means of a ruling machine. They must be always arranged spirally, and not parallel to the axis of the roller, or they would catch in the ink knife in the operation of printing. Cross hatching is generally employed. When the entire design is composed of hatchings or stipples, the rollers are termed padding rollers, the cloth being printed over its entire surface with a uniform layer of colour, and not in a figured pattern.

The engraving of this roller is conducted under a magnifying glass, the roller being mounted so as to rotate on the graving frame. When the process is completed the roller is polished with fine-grained sandstone and oil, and is punched with a number of coarse stipples outside the limits of the design, in order to prevent slipping during the subsequent pressure. It is then hardened by embedding it in sodium paste in the same box that was used for the softening treatment, heated to pale redness and quickly plunged into cold water several times in succession. As the roller, if too hard, would be liable to spring under the subsequently applied pressure, it is tested with chisels of different degrees of hardness, and, if found too hard, is rendered a little milder by reheating. Finally, it is scoured with loam and water, rinsed, and dried.

To produce the actual stamping roller, with the design in relief, from this molette, a steel cylinder, the peripheral measurement of which is a multiple of the first one, is softened, the two being then pressed tightly together by the aid of screw clamps and set in rotary motion. During this operation, whereby the metal of the softened cylinder is forced into the depressions of the hard one, the cylinder is strewn with a mixture of resin, fat, and wax. This mixture is also forced into the depressions of the matrix, and spreads thence over the raised portions of the patrix, so that when the latter is immersed in nitric acid only the unprotected parts are corroded by the acid, the result being to deepen the cuttings. The molettes are again clamped together and pressed, followed by another etching, the series of operations being repeated until the desired effect is completely produced. The stipples designed to prevent slipping are next cut away with hammer and chisel, and their place taken by shallow depressions serving the same purpose.

The finished patrix should be a little thicker in the middle than at the ends, because the latter always wear away quicker, and for this purpose the ends are tapered off by a succession of etchings, commencing at the extremities, after which the roller is finally hardened.

This roller is now employed to transfer the pattern to the actual printing roller, which must be turned down so as to correspond exactly to a multiple of the molette, and is then mounted so as to rotate on its axis, clamped in contact with the molette roller, and set in motion, slowly at first, but more quickly afterwards, plenty of oil being applied. When the design has been cut all round the printing roller, the molette is shifted by a distance exactly corresponding to the length of the pattern, and clamped on again, the whole series of operations being repeated until the full working width of the printing roller has been treated. The projecting portions are then ground smooth, and the roller is cleaned.

It being necessary that the ink should be removed as completely as possible from the raised portions of the cylinder, the surface of the latter must be absolutely true, since the colour would otherwise collect in any irregularities—other than those of the pattern—and dirty the fabric. To produce this perfectly plain surface the cylinder is slightly etched with nitric acid and then lightly ground, which will reveal the projecting portions by the contrast between their smooth surface and the dulness resulting from the etching. These prominences are removed by etching, the hollows being lacquered over and the cylinder dipped in nitric acid. Finally, the whole cylinder is gently ground. Faulty engravings, as well as old patterns to be replaced by new ones, are removed entirely by grinding.

Engraved designs can be produced on the molette or the printing cylinder entirely by etching. In the first place, the design is brought, by means of a camera obscura, in a five-fold state of magnification, on to a varnished zinc plate, and the details painted in their natural colours in order to facilitate recognition of the parts which are in association and have to be transferred to the same roller. The outlines are then punched out, their dimensions being diminished in a degree determined by experience, because of the tendency of the acid to enlarge them in the etching process. The reduction of the magnified design to its original dimensions in the course of transfer to the printing roller is effected by means of the pantograph, the stylus of which is moved over the outlines on the zinc plate, whilst the diamond engraving point which marks the pattern on the lacquered printing cylinder has an amplitude of movement only one-fifth that of the stylus. A sufficient number of these diamond points is provided to mark the pattern over the whole length of the printing roller at one operation. The roller is then etched in the usual manner, the lacquer washed off, and the etching gone over with the graving tool.

In printing on the cylinder machine the cloth suffers extension mainly in a longitudinal direction, the stretching progressing at each roller, so that on reaching the sixth roller it has attained about one-sixteenth of an inch. In order to counteract this tendency the rollers are made of different sizes (diameter); thus, in a four-colour machine, the first roller is a little smaller than the second and third (which are equal), whilst the fourth and last are a little larger than the intermediate ones. The disadvantage of this method is that the serial order in which the rollers come into action is arbitrarily fixed beforehand. In some works, rollers of equal diameter are used throughout, and the stretching is counteracted by special means, which, however, are not divulged by the users.

Setting and Working a Single-Colour Cylinder Machine.

The chief parts of the single-colour cylinder printing press (Fig. 37) are as follows: (*a*) the engraved printing cylinder;

(*b*) the backing cylinder; (*c*) the ink-duct; (*d*) the inking roller; (*e*) the scraper; (*f*) the heating or drying plates.

In this figure the goods to be printed are indicated by *g*, the backing cloth by *i*, and the intermediate cloth by *h*. The path taken by the goods is shown by the arrows, the cloth being unwound from the roller *k*, passed between the printing and the backing cylinders, where it is printed, and then led alternately upwards and downwards between drying plates, or dried by circulating through an enclosed hot chamber *o*, and finally delivered in folds at *l*.

Successful printing depends on several points of detail, including chiefly—a properly compounded printing colour and well-prepared printing cylinder being presupposed—the accurate working of the scraper. As already stated, this organ serves to scrape off the colour from all the unengraved parts of the cylinder. It consists of a thin steel blade which is pressed against the printing cylinder, in the direction of rotation of the latter, by means of a weighted lever placed on one side, and receives reciprocating motion by the action of an eccentric rod actuating a bell-crank lever. The upper edge is ground sharp, though in some cases (*e.g.* striped patterns) a rounded edge is preferred. When acid colours are used, the scraper must be protected by a coating of varnish. In some cases a second or counter scraper is provided (*m*, Fig. 37), mounted in the opposite direction to the movement of the cylinder, its use being to remove any fine nap that has become separated from the fabric, and prevent the same from getting into the colour; this scraper is immovable.

The backing or pressure cylinder serves as a solid abutment for the printing roller. To make this pressure elastic, the backing cylinder is mounted in adjustable bearings, which can be moved up and down in grooves by the aid of a train of levers, the pressure on the printing cylinder being increased at will by weighting the levers. The necessary accurate parallelism of the two cylinders is secured by the aid of strong screws, and the elasticity of the pressure is increased by covering the backing cylinder with several layers of tightly stretched printer's blanket. The same object is effected by the backing cloth

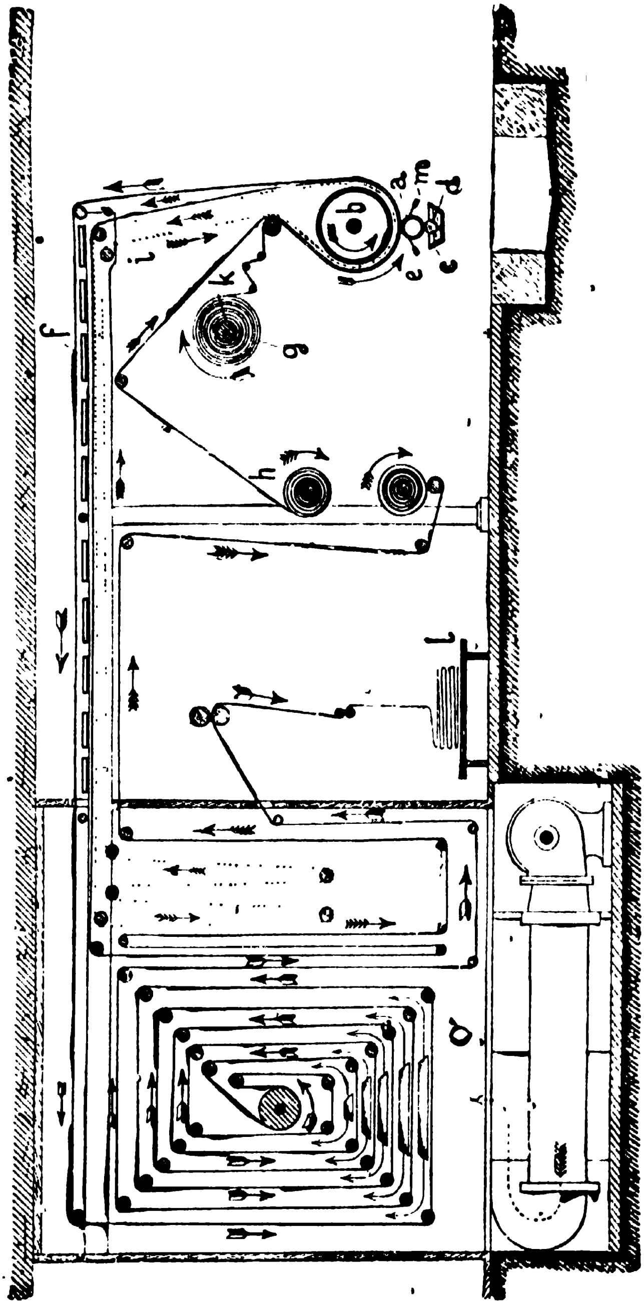

FIG. 37.

(*i*, Fig. 37), an endless cloth composed of several layers of stout cotton fabric fastened together with caoutchouc; in this case, as also in the blanket clothing the cylinder, all wrinkles must be entirely avoided. The intermediate cloth, which keeps the backing cloth from becoming stained by the printing colour, is of rough gassed cotton fabric, which after a while is cleansed by bleaching. It runs between the cloth to be printed and the backing cloth. After passing through the machine all three cloths are dried by being led between hot plates (*f*, Fig. 37), which are generally placed in the rear of the machine; or by circulating through a closed hot chamber. The intermediate cloth is afterwards washed and used over again; though a better way is to keep this cloth in continuous motion, washing it by passage through a water-trough and roller brushes, after leaving the press, and then drying it on a hot cylinder.

In printing, the printing cylinder is set in motion by toothed gearing, and carries the backing cylinder round with it. A piece of the intermediate cloth is first passed between the cylinders, and the extra piece, attached to the cloth to be printed, is also passed through and fixed on to the guide bands leading to the drying apparatus. Both the goods and the intermediate must be quite straight, free from folds, and passed into the machine at a certain tension, which is attained by applying weights to the axes of the rollers on which these cloths are wound, in order to ensure uniform pressure against the bearings.

The pull exerted by the two cylinders on the goods and intermediate cloth in order to unwind them from their respective rollers must never be so great as to damage the fabric, and should remain as uniform as possible during the operation of printing—an object attained by the aforesaid weighting.

The task of the printer consists in watching the fabric as it passes through the machine, so as to immediately detect any defects in the printing. This is arduous work, and requires the aid of a good light to perform successfully, on which account the machine is generally set up in front of a large window. As soon as the first yard has passed through the machine the printer must satisfy himself, by turning up the edges of the stuff, that the pressure is equal on both sides; the colour should show through at the back to an equal degree on both edges. The defects arising in printing generally originate in the scraper. Thus, if any solid substance, for example, gets between the scraper and the printing cylinder and lift up the former a little, the scraper will cease to act for that instant and will thus leave a cross stripe of colour on the cylinder Should the solid obstruction (*e.g.* a grain of sand) remain, the scraper will be prevented from acting on the colour at that particular spot, and a longitudinal stripe of colour will therefore be formed. Similar stripes are also produced when the scraper has become worn in places through constant friction against the engraved roller. If the edge of the scraper has not been ground sharp enough, the impression of the outlines will be fuzzy instead of clear. When the printing cylinder is not true, the scraper will not touch such parts as are below the general level.

Another cause of defective printing may reside in the colour, especially when this does not properly come off on to the cloth, but remains in part in the channels of the engraved surface. When such is the case, the inking roller must be replaced by a roller brush. In the case of colours, like chrome yellow, that exhibit this defect in a higher degree, a second stationary brush must be fixed up in front of the printing cylinder.

In any event, as soon as any defect in the printing is noticed, the printer must stop the machine and remove the cause. As the scraper is the chief cause of defects, this tool must be reground after a certain number of pieces have been printed.

When a change of colour is made, the printing cylinder, scraper, and ink-duct must all be thoroughly cleaned, the best plan being to keep separate sets of brushes and cleaning cloths for blue, red, and in fact for each different colour used.

Setting up and Working a Multiple-Colour Machine.

Although cloth-printing machines have been constructed to print as many as twenty, twenty-five, and even more colours, it is not usual to go higher than twelve, since the heavy pressure to which the fabric is exposed necessitates the employment of stronger colours (*i.e.* richer in pigment). The machines most frequently are two to six-colour presses.

The multiple-colour machine has a separate printing cylinder, ink-duct, ink-roller, and scraper, for each roller; a three-colour machine, therefore, having three printing cylinders, three ink-ducts, three inking rollers, and three scrapers. On the other hand, there is only a single backing cylinder, backing cloth, and intermediate cloth, as in the single-colour machine.

In this case the arrangement for producing elastic pressure is somewhat different. The backing cylinder, the size of which depends on the number and size of the printing cylinders, is mounted on bearings that can be raised and lowered by means of screws, but it is kept fixed during printing. The set of levers mentioned in the single-colour machine acts in this case on the lowermost printing cylinder, the others being pressed against the backing cylinder, either by the aid of screws fitted with rubber rings or else by means of levers.

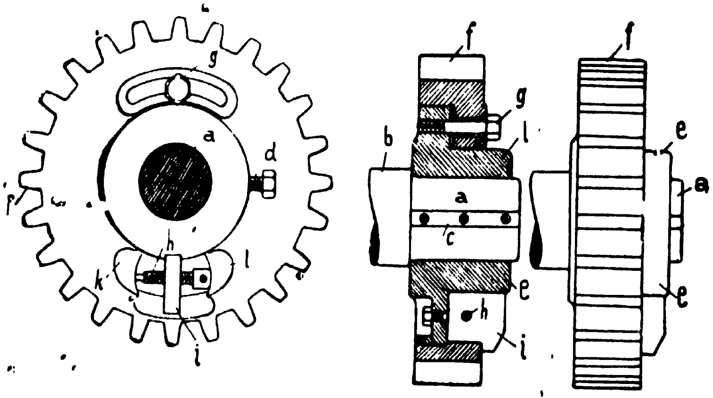

Fig. 38.

The principal difference in the method of working the two classes of machines consists in the method of producing the register, *i.e.* the proper relative adjustment of the various parts composing the pattern. For this purpose a special device is required—the wheels mounted on the different roller spindles, which are driven by a pinion in the centre, being fitted with a device which enables any difference in the movement and situation of the individual rollers to be compensated; these wheels are therefore called register wheels. A sleeve *e* is fastened on the trunnion of the printing cylinder *b* by means of the spring key *c* and set screw *d*, and is loosely connected with the driving-wheel *f* by means of the screw *g*. A screw *h* passes through the lug *i* on the sleeve *e*, and rests at both ends against two half-moon lugs *k*, *l* on the printing cylinder wheel. On turning the screw in one or the other direction by means of a key-pin passing through the head (which can be done whilst the machine is running), the sleeve *e* is moved in an axial direction and imparts a similar movement to the printing cylinder, so that in this way the rollers can be brought into register when either too far ahead or behind. It is, however, necessary to have the register approximately correct before starting, and this is effected in the following manner:—

The lower roller is first put into position and set parallel to the axis of the backing cylinder, the other rollers being then put in and set parallel to the first. The cylinders having been marked by the engraver at the place where they correspond, that on the first roller is now marked with chalk, and the machine is started slowly, only the intermediate cloth being run through at first. This chalk-mark prints off on the intermediate cloth, and the resulting impression should exactly coincide with the corresponding marks on the other cylinders if the register is correct. This will rarely if ever be the case at the outset, and it will be necessary for the printer to adjust the register either by a lateral movement of the rollers or by means of register wheels. This having been approximately done, the ink-duct is filled with colour, and a remnant of cotton fabric is run through the machine, the resulting impression showing what additional correction is required to obtain a perfectly accurate register.

In beginning to print, the machine is first run very slowly; and the printer must give careful attention to all the points already mentioned in connection with single-colour printing; in addition to which he will have to look after the register all the time the printing continues, since slight alterations of register are constantly occurring, as a result either of slight modifications in the tension of the fabric, or from other causes. This work of adjustment can always be carried out while the machine is running, stoppages being avoided as much as possible, since they are liable to produce light streaks on the goods, in consequence of the colour running out of the engraved parts near the point of contact with the material.

An unavoidable inconvenience in multiple colour-printing on the cylinder machine is, that the colour cannot be completely removed from the smooth parts of the cylinders by the scraper, and consequently small particles of colour are left on the material, and get mixed with the next following colour. On this account great care must be taken to use the most delicate colours (*e.g.* pink, yellow, pale blue), first leaving those capable (like black) of doing most damage until last. To prevent a clouding of the colour by preceding colours, a so-called water-roller is placed between each two-printing cylinders. This consists of a smooth cylinder, provided with a scraper, and fed with a thin solution of tragacanth or gum. Sometimes the final printing cylinder is followed by a smooth cylinder, which presses the colour into the material. This is employed when it is desired to have the pattern on thin material shown up about the same on both sides, so that the corresponding parts exactly coincide, as in the duplex printing machines, which will print up to eight colours on each side, the method of working being shown in the diagrammatic sketch (Fig. 39).

Really the machine consists of two machines, each having its own backing cylinder, backing cloth, and intermediate cloth. The engraving on the rollers of the one machine is to those of the other as image and reflection.

Before beginning to print the actual fabric, about thirty yards of material are run through the machine to enable the rollers to be adjusted and set in register. For the latter purpose all the rollers of each separate machine are connected with a large register wheel, so that the whole of the rollers can be adjusted to the same extent by a single register screw. After the impression the stuff is passed over a water-roller. Printing on both sides is more particularly employed for the production of curtains and upholstery goods and calico-printing.

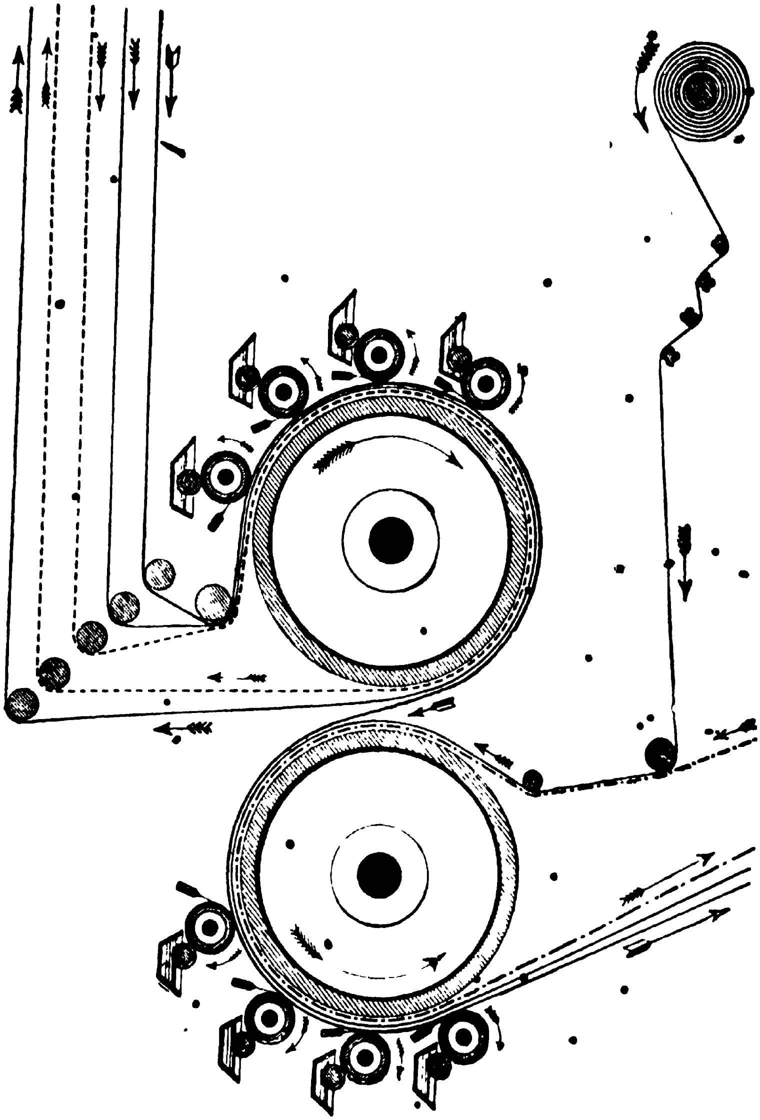

FIG. 39.

Intermittent printing machines ("jumpers") are used when the details of the pattern are repeated at such wide intervals (longitudinally) that the rollers would have to be of unmanageable dimensions. The machine introduced by Pickup and Knowles of Pendleton has rollers of ordinary diameter mounted in such a way that they make intermittent contact, for a certain number of revs., with the fabric running through the machine, and then move back automatically, for a definite interval, to give place to others.

In the pile method of printing flannels and fabrics with raised patterns the printing rollers are merely brought into loose contact with the surfaces to be printed.

CALICO-PRINTING.

The goods intended for calico-printing must be first bleached in the most complete manner possible. Some colours are printed on prepared fabric; others without this preliminary treatment. The preparation consists in padding the fabric in a solution of Turkey-red oil (about 9 oz. per gallon), followed by drying. Some colours, especially alizarine red and rose-red, show up much brighter on prepared stuffs, and this property of Turkey-red oil is also utilised to revivify certain colours that have suffered under treatment subsequent to printing (*e.g.* by chroming), the goods in this case being padded with Turkey-red oil, dried and gently steamed for a short time.

The different styles of calico-printing are as follows:—

1. Reproduction of the pattern by direct printing.
2. Combined dyeing and printing.
3. Discharge style printing.
4. Reserve style printing.

1. Reproduction of Pattern by Direct Printing.

In this case the principal thing to be considered is the colour, its preparation, and fixing.

The printing colour contains a solution of suspension of one or more dye-stuffs, solvents such as alcohol or organic acids, mordants, tannin, thickening material, and occasionally other substances as well.

The dye-stuffs must be always of the same strength, and consequently have to be first tested by a sample printing. Each dye-stuff is dissolved separately, the solution being used only in a filtered condition. Dye paste should be carefully stirred up before being sampled; and solid dyes must be reduced to the finest possible state of division for use.

The mordants are, for the most part, salts of acetic, lactic or formic acid, which are prepared in a concentrated form by the printer, and kept in stock, it being difficult to increase the concentration, though dilution with water can be effected as required. The fixing agent used is tannin, generally dissolved in water and acetic acid.

Oleic acids (Turkey-red oil) are frequently added to brighten colours, but are not used for fixing. Both the mordant and the fixing agents must be tested by an experimental printing, to determine their quantitative relation to the dye and influence on the shade and brightness.

A fixing agent of special character is albumin,[1] inasmuch as it is also a thickener. For bright colours egg albumin is used, but for all others the less pure but much cheaper blood albumin, which is prepared by evaporating defibrinated blood in vacuum pans. To prepare the solution of blood albumin, cold water must be used, a typical method for large quantities being to distribute 66 lb. of albumin in 6½ gallons of water and leave it to steep for twenty-four hours, after which 1¼ gallons of oil of turpentine are stirred in (to prevent frothing in printing) and ½ gallon of ammonia to keep the solution from turning sour.

When the fabric printed with albumin is exposed to heat (*e.g.* by steaming), the albumin coagulates and adheres to the fabric as an insoluble mass which fixes the colour with which it is incorporated.

The adjuncts to printing colours are acetic acid, tartaric acid, sodium chlorate, olive oil, fats (tallow, lard, etc.), turpentine, glycerine, and sal ammoniac; other adjuncts being used only in exceptional cases. Acetic acid serves to dissolve the dye-stuffs and colour lakes, a purpose also served by the less frequently used tartaric acid. Sodium chlorate is added as an oxidising agent to some colours—aniline black, logwood, etc. Olive oil softens the colour and facilitates printing, the same effect being produced by other fats. Turpentine is added to some colours to prevent frothing in the ink-duct.

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[1] It has been proposed to replace albumin by the cheaper glue or gelatine rendered insoluble with formaldehyde. In such event the colour must be mixed with glue and formaldehyde, printed and steamed.

On account of its non-drying properties, glycerine forms a useful adjunct to many colours, especially such as are prepared with gum or albumin; it prevents frothing, softens the colour, and keeps it from drying on the printing cylinder. Sal-ammoniac, being hygroscopic, is added to colours which it is advisable to prevent drying quickly, *e.g.* aniline black.

Thickening Agents.—These consist chiefly of wheat starch, flour, baked starch, gum, and albumin. Wheat starch is perhaps the most frequently used for thickening in calico-printing. The paste is prepared by stirring up the starch to a thick pulp, with a little water, and gradually adding more water until a thin milk is produced, whereupon the rest of the water is added all at once, and the whole is boiled until the thickened paste begins to turn a little thinner. It is then cooled and stirred until quite cold, to prevent it getting mouldy.

Boiling is effected in pans of the type shown in Fig. 40. Steam heat is used, the steam being admitted through *f*, *g*, and *h* in the steam jacket *b*, the excess and condensed water being drawn off at *c*. When the boiling is finished, the steam is shut off, *c* is opened, and cold water is run into the jacket from *i*, through *m*. Stirring is effected by so-called planet stirrers, *l*, the stirring paddle, in addition to rotating on its own axis, also describing a circular path round the inner wall of the pan. To empty the pan the stirring apparatus is uncoupled at *t*, *v*, and the pan is tipped about on its horizontal axis after the paddles have been taken out. This thickening material is generally prepared in two strengths, the one containing 100 parts, the other 150 parts by weight of starch per 1000 parts of water, the strength being accordingly expressed by $\frac{100}{1000}$ and $\frac{150}{1000}$.

Wheat starch paste is unsuitable for colours containing strong acid or some strong acid salts, which act upon it and

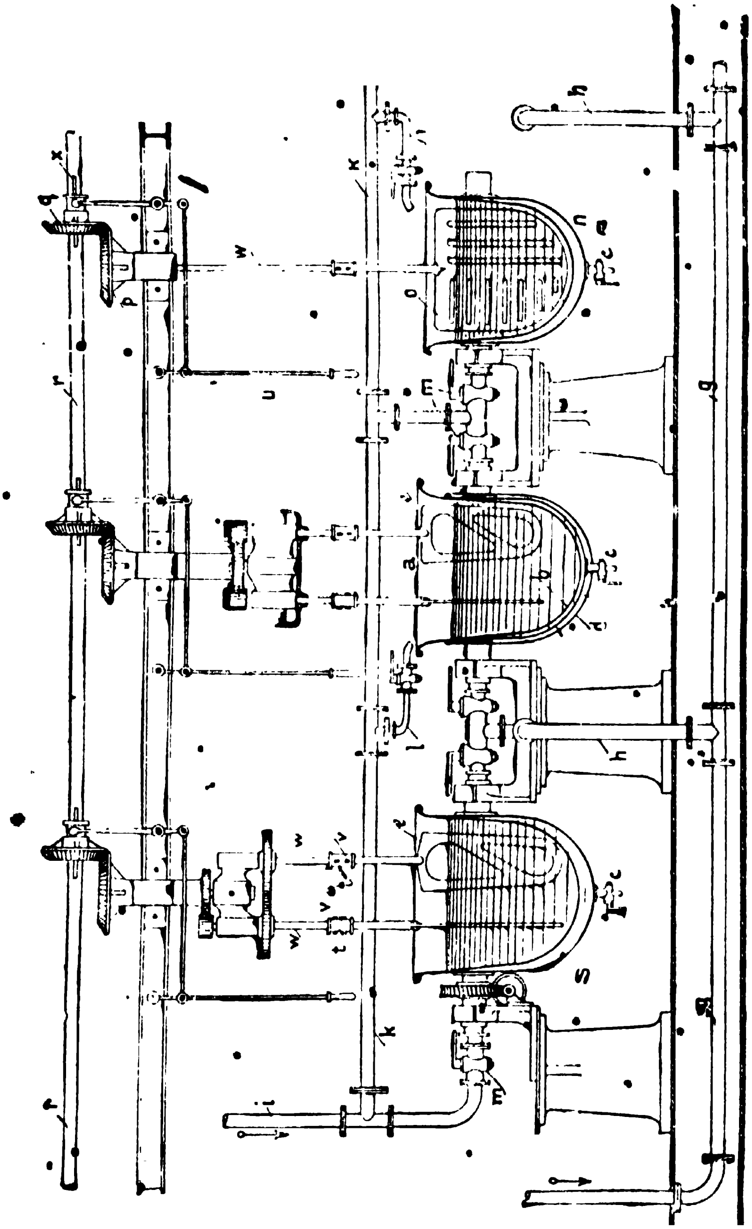

FIG. 40.

convert it into dextrin, which forms a thinner solution. Acetic acid, however, produces no change, even on boiling.

As a rule, the starch is merely tested for its thickening properties, and for the presence of insoluble foreign matters such as sand, etc. In the first test, starch of acknowledged quality is employed for comparison, a thin paste of equal concentration being prepared from each, and their consistence compared by allowing them to drop from a spatula. To test for insoluble matters capable of forming scraper streaks in printing, the starch is stirred up to a thin milk with water, whereupon the solid foreign matter will quickly subside and can be examined after the liquid is poured off.

Two kinds of roasted starch are prepared, namely, light and dark, the former being a light brown powder, which is mixed with water in the proportion of 7 parts to 5, 5 additional parts of water being then added, and the whole boiled for about two hours. To the same class also belong a number of white products, *e.g.* dextrin, prepared by heating wheat starch to about 100° C. with dilute acid; British gum, a dextrin from rice and maize starch; Leio gum, a roasted potato starch, and crommelin and *ly-chow*, which are similar products. These light roasted starches do not thicken so strongly as starch itself, but are very useful for thin colour. They are soluble in water in all proportions.

Dark roasted starch is prepared by roasting starch at about 200° C. In consequence of excessive roasting, it often contains a brown insoluble substance which would choke up the engraving, and must therefore be kept out of the printing colour. To determine the value of starch of this kind, a small quantity, about 10 grms., is dissolved in half a litre of water, and left to stand awhile in a graduated cylinder, the insoluble sediment being then measured. The utility of the sample is in inverse proportion to the amount of the sediment.

This dark roasted starch has only about one-fifth to one-sixth the thickening power of wheat starch. In consequence of the sugar content it may serve to retard the oxidation of certain dye-stuffs or iron mordants. When printed it does not penetrate so deep into the fibre as unroasted starch; also when dried it is more readily softened by water, and can therefore be more easily washed out of the fabric than the latter. It is very useful for strongly acid dyes, and is really the only suitable thickening for strongly alkaline dyes. In these cases, roasted maize starch is generally used. The solution is prepared by stirring up 10 parts of the starch with 5 parts of water, then adding another 5 parts of water, and boiling the whole up for two hours. All the different gums used are chiefly made of gum-arabic, tragacanth, and Senegal gum. Latterly, soluble gums, generally prepared by boiling the insoluble gums under pressure, have also found employment.

Gum-arabic is one of the oldest thickenings used, and is particularly suitable for pale clear tints. Both raw and roasted starch cause the fibre to look darker and stronger than when printed with gum thickening. The colours thickened with gum dry quickly and contract the material, on which account gum is unsuitable for printing mordants, because in this case the colours do not show up full when subsequently dyed.

The contraction of the material by gum can be prevented by adding a little pipeclay. Gum-arabic being dear, it is where-ever possible replaced by light roasted starch or tragacanth. Frequently it is used for colours that must be applied in concentrated solution, in which case it is strewn in the form of powder. The solution of gum-arabic is prepared by stirring up the gum with boiling water, and then either boiling or leaving to stand until dissolved. Should the solution be lumpy, an adulteration with insoluble gums is indicated. The usual strength of the solution is either 1000 parts or 800 parts per 1000 of water. As dissolved gum readily falls a prey to acid fermentation, the solution should be prepared in small quantities only, and stored in a cool place. Fresh solutions of gum should not be put into vessels containing remnants of old solution.

Senegal gum, although very cheap, is not in much favour; it sticks too fast to the fabric, and therefore can only be used with colours that will stand vigorous washing. It imparts a certain smell to the material.

Tragacanth is a very important thickening, and is used in a thick mucilage or as tragacanth water. The thick mucilage is prepared by suffusing tragacanth with hot water (60 parts to 1000 of water), leaving to stand for twenty-four to twenty-eight hours, and then boiling in a closed cylinder until the mucilage has become perfectly homogeneous (four to six hours). The thickening most frequently employed, especially for tannin colours, is a mixture of equal parts of wheat starch paste and tragacanth mucilage ($\frac{80}{1000}$). This is sometimes known as mark 1/1. The thickening power of all these substances is tested in exactly the same way as with wheat starch; in some cases, especially gum-arabic, they are also tested to see if they cloud the thickening colour, for which purpose a sample print is made with a light colour, such as pale blue and methylene blue.

These thickenings are mostly prepared separately, and then added to the corresponding colour solutions and adjuncts before use. A few of the readily soluble substances are sometimes mixed in the solid state with the warm thickening; fats must always be boiled in mixing; dyes and mordants, on the other hand, must only be mixed cold, since otherwise precipitation might occur through the formation of lakes. Formerly the printing colours, especially those containing starch, were generally boiled, *i.e.* the starch was mixed not only with water, but also with the dye-stuffs and several necessary adjuncts (except mordants), and then boiled for an hour or longer in the same pans as used for making wheat-starch paste (Fig. 40).

Apparently the sole object of this in most cases was to combine the gelatinisation of the starch and the mixing with the other ingredients in one operation. This is still done when a better incorporation of the ingredients can be secured by boiling them all together, *e.g.* in the case of colours containing dye-wood extracts. Since most printing colours contain acetic acid and olive oil, these substances are very often added in preparing the starch paste, from $\frac{1}{10}$ to $\frac{3}{10}$ of a gallon of 6° B. acetic acid—according to the colour—and about 3½ to 7 oz. of olive oil per gallon of thickening being used. In the case of starch-tragacanth thickening, the finished tragacanth mucilage is also boiled over again.

All thickenings must be strained for the removal of lumps and solid particles, and this is effected either by putting them in a bag strainer and forcing them through the meshes of the fabric by pressure and twisting, or placing them on sieves and working them about with brushes by hand or mechanical appliances in imitation of hand labour, in order to rub them through. It is also advisable to strain the finished printing colour after the addition of the thickening material to the other ingredients.

All these thickenings and other dissolved substances used in preparing the printing colour are measured out in graduated copper vessels, which is quicker than weighing; dye-stuffs and dye pastes, however, are weighed. The finished colour is stored in earthenware vessels or wooden casks, which are marked to prevent confusion. If a lighter shade of an already prepared printing colour is required, it may be obtained by diluting the latter with a given weight of the same thickening that was originally employed; for example, a red printing colour thickened with starch paste and numbered "red 100" is reduced with three parts of the same starch paste; this reduced or diluted colour will then be numbered "red 100⅓". In diluting tannin colours the diluent thickening should receive a sufficient addition of tannin to contain approximately the same percentage of tannin as the printing colour itself. This is necessary because the thickening material and the cotton both absorb certain quantities of tannin.

To calculate the cost of a printed article, the amount of colour consumed in printing a single piece must be taken into consideration as well as the price of the printing colour itself. This is done in the following simple manner:—

The colour is weighed before use, and again after a certain number of pieces have been printed, the difference in weight giving the amount consumed.

Employment of Mordant Dye-Stuffs.

Thanks to their fastness, the mordant dyes play a predominant part in calico-printing. They are all so-called "steam" dyes, because the aid of steam is necessary to effect the combination of the dye with the mordant, the formation of the colour lake, and the fixing of the latter on the fibre.

Alizarine is the most important of the series. For red and rose it is used along with alumina mordants (with or without tin mordants); with iron mordants for violet, and with chrome mordants for Bordeaux and brown. In the case of red and rose the goods must always be prepared before printing, as otherwise the colour will come out dull and impure. The blue tinge alizarine marks are used for rose, whilst for red those chiefly consisting of flavopurpurine are taken.

Of the other mordant dye-stuffs the following are chiefly used: alizarine viridine, alizarine green, etc. (as chrome lakes), for greens (cœruleine, formerly so important, having now receded into the background); quercitron and buckthorn berries (as tin, alumina or chrome lakes) for yellow and brown; alizarine yellow GG, R, Oriol yellow, calico yellow (Gy), chrome yellow, diamond flavine, etc. (as chrome lakes) for yellow; alizarine orange, with alumina for orange, and with chrome for brown. Other less stable dyes are also used for orange: chrome orange, diamond orange, etc. For violet (apart from alizarine-iron): gallocyanine, galleine (as chrome lakes), alizarine bordeaux (with alumina), alizarine garnet, alizarine heliotrope, modern violet, alizarine cyclamine (with chrome), etc. For blue: alizarine blue (with chrome, nickel or zinc), alizarine cyanine, gallamine blue, dolphin blue, celestine blue, philochromine G (with chrome), etc.; for grey: alizarine black (with chrome); for black, logwood. The last named is also used for mixed colours (various browns). Redwood and catechu are now rarely employed in calico printing.

Without going into special details, not much can be added to what has already been given as to the preparation of the printing colour. The alizarine dyes are mixed with the thickening, in the cold, whereas dye-wood extracts are generally boiled in the course of preparing the thickening. For producing light shades, the printer usually prepares diluted pastes and extracts from the concentrated commercial articles. The proportions of ingredients taken vary in different establishments; the principal thing is to have the correct ratio of dye-stuff to mordant, and in this respect it is always preferable to have too much mordant than too little, because in the latter case the unfixed dye is loosened from the fibre in the subsequent washing and dirties the material. Acetates were almost the only mordants used at one time, but now lactates, formates and bisulphites are employed as well. The chrome mordants are the most important, but alumina, nickel, iron, and tin mordants are also used.

Employment of Basic Dye-Stuffs.

An important part is also played by the basic dyes in calico-printing, the following being those most in use: ordinary auramine and the G marks; thioflavine, auracine (By), methylene yellow (M.L.Br.), chrysoidine, phosphine, patent phosphine, flavophosphine, acridine orange, tannin orange, safranine, fuchsine, rhodamine, irisamine, rhoduline, pyronine, induline scarlet, brilliant green, malachite green, methyl green, methylene green (the fastest basic green), methylene blue, new methylene blue, ethylene blue, turquoise blue, cresyl blue, capri blue, Nile and glacier blue, Victoria blue, printing blue, acetine blue, methyl violet, methylene violet, tannin heliotrope, etc. Some of them exhibit a tendency to encrust on the unengraved parts of the printing cylinder, and in such event a bar covered with flannel must be employed at that part of the cylinder where the counter-scraper is usually placed.

The printing colour consists of three portions, all of which are generally prepared separately, *i.e.* the thickening—mostly wheat starch and tragacanth thickening, 1/1 gum water being often used for delicate tints; a solution of the dye in acetic acid and water, or acetic acid and alcohol; and a solution of tannin in acetic acid and water. In recent times, acetic acid has been advantageously replaced by formic acid for certain dye-stuffs. For some colours tartaric acid, or ethyl-tartaric acid, is added as well; this last-named acid, acetine, formine, or levulinic acid, being employed as a solvent in the case of the indulines. These additions, acetine in particular, have a beneficial action on most of the basic dyes. In printing the ground of a pattern it is advisable to add hydrosulphite to the printing colour. Colourless tannin should be used for bright light tones, especially for light blue. Most of the basic dyes show up better when printed on prepared cloth.

The basic dyes are used in a special manner for the production of the so-called "Lucca" goods, which constitute an imitation of Indian shawls. The goods are prepared by padding with a solution of sodium stannate thickened with a solution of casein in water and borax. The dyes are mixed with albumin or various metallic salts, such as aluminium acetate and magnesium acetate; with sodium arsenite and aluminium acetate; with arsenicated glycerine, etc., and a thickening material, and fixed by steaming.

All the printing colours prepared with basic dyes are steam colours, steaming being indispensable to fix them on the fibre.

Employment of Albumin Dye-Stuffs.

Many of the mineral pigments, such as ultramarine, vermilion, chrome yellow, orange chrome, chrome green, various ochres, and lampblack paste (for grey, shaded with ultramarine), being insoluble, cannot be fixed on the fibre in any other way than by mixing them with albumin before printing, the fixation of the colour and the recovery of the albumin being then effected by steaming. Hence these colours also are "steam colours". Occasionally other colours capable of employment in other ways can also be used as albumin colours, *e.g.* buckthorn-berry tin lake, erythrosine—precipitated from its solution by sulphuric acid, and mixed with albumin—as also solutions of basic dyes, such as methyl violet and fuchsine.

In order to economise the expensive ingredient albumin, it is generally replaced in part with tragacanth mucilage or starch paste: naturally, the lower the proportion of albumin employed, the less satisfactorily will the colour be fixed.

The beauty of the mineral printing colours varies directly with the fineness of division, for which reason it is the general practice to grind the commercial colours (chrome yellow and orange chrome pastes) for a considerable time, in association with a little dissolved gum, in indigo mills. In printing with these colours, the usual inking roller is replaced by a roller brush, and frequently a counter brush must be used as well.

Ultramarine, being difficult to moisten, must be converted into paste with a little alcohol. In using this pigment it must not be forgotten that it is easily decomposed by acids.

Chrome yellow and orange chrome are printed in association with a salt of cadmium, the object of which adjunct is to counteract the tarnishing effect of sulphuretted hydrogen (PbS) by forming a yellow sulphide.

Owing to their high cost the use of albumin colours is confined almost exclusively to indigo discharge style printing.

Employment of Direct Dye-Stuffs.

Of these dyes, which play such an important part in cotton-dyeing, only a very small number are used, and that, too, for the production of light grounds. These comprise chrysamine, chloramine yellow, brilliant geranine, diamine pure blue, etc. For the most part they are simply mixed with the dressing preparation and applied to the material therewith.

They are also used for printing by sliding contact, and for the production of coloured crépon effects, for which strongly alkaline printing colours are employed.

Employment of the Developing Dye-Stuffs.

The method of applying the ice colours is the same as in dyeing, the fabric being prepared with β-naphthol, dried, and printed with the thickened solution of the diazotised amine.

The instability of the diazo solutions makes itself felt here even more than in dyeing. All these colours have the defect of being unable to stand steaming, and being therefore unsuitable for mixing with steam colours. Nevertheless they play a still more important part in calico printing than in dyeing, especially since the introduction of the stable hydrosulphite preparations.

Nitroso-blue, introduced by the Höchst Farbwerke in 1898, belongs to the class of colours produced by condensation on the fibre. It is obtained by condensing nitrosodialkylanilines with phenols, and is an oxazine. The most important mark is MR, obtained from nitrosodimethylaniline and resorcin. Aqueous solutions of the two components (the first named as a chloride) are printed in association with tannin (the amount of which has a great influence on the resulting shade), oxalic acid, sodium phosphate (to protect the cotton-fibre from the hydrochloric acid) and a thickening medium; dried, developed in the Mather-Platt, fixed with antimony, and finally lightly soaped.

On account of its cheapness, fastness, and the ease with which it can be reserved, it has found great favour for various articles, especially raised, winter goods.

Aniline black, having already been fully described as oxidation black, requires little additional mention here. The same mixture as before is employed, and, being suitably thickened —preferably with dextrin—is printed on the fabric, the black being then developed just as in dyeing. In order to minimise the injurious effect produced by the acid, a portion of the aniline is used in the free state as aniline oil. When the goods are first printed with a lead salt, for the production of chrome colours, the aniline chloride is replaced by aniline nitrate, since otherwise lead chloride would be formed, and would incrust the scraper of the black roller. Also by using the nitrate less aniline is consumed.

For printing aniline black, vanadium or copper sulphide is used.

The vanadium solution is prepared by dissolving 20 grammes of commercial ammonium metavanadate in 100 c.c. of hydrochloric acid and 200 c.c. of water, the solution being warmed with commercial bisulphite until a blue coloration is produced and solution is complete, whereupon the whole is diluted to 20 litres, which then contain 1 gramme of ammonium vanadate (as chloride) per litre (H. Schmidt).

The copper sulphide paste is prepared by mixing 11 lb. of flowers of sulphur with 4½ gallons of caustic soda (36° B.), and leaving to stand for several days until quite dissolved, this being assisted by warming if necessary. On the other hand, 53 lb. of copper sulphate are dissolved in 55 gallons of hot water, and mixed with the sulphur solution, the resulting precipitate being collected on a flat linen filter and well washed with hot water. The precipitation must not be effected from concentrated solution, or the copper sulphide deposited will be coarse in grain and carry down with it some of the copper sulphate, which will then decompose the padding liquor quickly (Kielmayer). The copper sulphide paste must be kept away from the air, being stored under a thin layer of ammonium sulphide. In the event of any oxidation, it must be placed on a filter and washed with ammonium sulphide and water.

The amount of oxygen carrier used depends on the quantity of aniline and oxidising agent, and on the manner in which the subsequent developing is conducted, the rate of development being quicker as the amount of oxygen carrier is increased. According to Witz, 1 part of vanadium protochloride is sufficient to convert 200,000 parts of aniline salt into black; but in practice the quantities used are much larger, varying from $\frac{1}{10}$ milligramme to several milligrammes per litre of padding solution. The proportion of sulphur paste—which is about 30 per cent. strength—is about 10 grammes per litre.

The action of vanadium is attributed to the formation of a very unstable chlorate; and that of copper sulphide to the formation of a copper salt.

Sometimes a so-called aniline steam black is used, the colour being developed by steaming. These colours are either compounded in the same way as Prudhomme black, or else contain yellow lead chromate instead of ferrocyanide. Moreover, in light patterns, an ordinary aniline black can be developed by steaming, in which case the printed goods are first developed in the oxidising chamber, then passed through ammonia vapour and entered in the warmed and closed steamer—on the floor of which one or two pans filled with ammonia have been placed —where they are steamed in the usual way for about a quarter of an hour.

Aniline black always corrodes the scraper to some extent, and this should therefore be ground afresh after a certain number of pieces have been printed.

The history of the evolution of aniline black is very interesting:—

The first aniline black printing colour was prepared by John Lightfoot in 1863, and consisted of aniline, hydrochloric acid, acetic acid, potassium chlorate, cupric chloride, sal-ammoniac, and starch paste. When this black was printed without copper, by the aid of a woollen roller, it did not develop at all, but the black showed up after being placed in contact with a metal plate for a short time, from which behaviour Lightfoot concluded that metals were essential to the development of the black. However, the employment of soluble copper salts proved a failure, owing to the formation of a precipitate of aniline black within the colour itself. Subsequently attempts were made to obviate this by impregnating the goods with a solution of copper sulphate by padding, and employing a colour, free from copper, for the printing. In this case, however, the white of the fabric must be cleaned by treatment with ammonia. Finally, recourse was had to insoluble copper salts, like copper ferrocyanide or copper hydroxide; in fact, the recommendation made by Lauth in 1864 to use copper sulphide is still followed at the present time. For hand-printing, however, copper sulphate must be retained, because the paste preparations readily incrust the block.

It is now known that metals are not essential for the development of aniline black; all they do is to decompose the chlorate, which object can also be effected by the aid of acids.

A further important advance was the introduction of aniline tartrate, as a substitute for the chloride, by C. Koechlin in 1865, thus making it possible to print even the finest fabrics with aniline black without any risk of corrosion. The quantity of tartaric acid employed to dissolve the aniline is between that required for the formation of the neutral salt, on the one hand, and the acid salt on the other. Without sal-ammoniac it is impossible to obtain a good black; and the action of this salt is explained by the assumption that, by temporarily producing aniline chloride, it helps to start the oxidation.

An aniline black produced with tartaric acid requires much more chlorate—70 per cent. and over—than the ordinary black with aniline chloride. This consideration and the use of tartaric acid render this colour so dear that it is now seldom used.

A further very important improvement was the introduction of Prudhomme black, which does not attack the fibre, and, by reason of its slowness in developing, enables reserve styles to be obtained on an aniline black ground. Still another is the diphenyl black base from which a perfectly non-greening black can be obtained.

Another colour produced by oxidation on the fibre is the paramine brown, already mentioned. This is a very good substitute for catechu, which has the disadvantage of clogging the printing blocks and rollers, and of requiring to be chromed in developing. Paramine brown is largely used, especially for raised fabrics.

The mineral colours developed on the fibre in calico-printing are the same as used in ordinary dyeing.

The usual plan in the case of chrome yellow and orange chrome is to print with a suitably thickened mixture of lead acetate and nitrate, and then treat exactly in the manner described in the previous chapter. Iron chamois is seldom used. Berlin-blue is never employed alone in calico-printing, but only as an adjunct to various printing colours, *e.g.* logwood black, and with mordant dyes or tannin dyes for olive-green and brown shades, by mixing potassium ferrocyanide therewith, Berlin-blue being then formed, in the presence of acids, by the heat of the steam chamber.

A "steam chrome yellow" and "steam orange chrome" are produced in printing with lead acetate and nitrate in conjunction with barium chromate paste, and then steaming.

A manganese bistre can also be produced as a steam colour by printing a mixture of sodium or potassium bichromate, manganous chloride, and sodium acetate, the oxidation being effected by steam.

Employment of the Sulphur Dye-Stuffs.

The employment of sulphur dyes in calico-printing was greatly impeded by their low resistance to bleaching and by the corrosive action of the alkali-sulphide printing colour on the copper rollers. To remedy this latter drawback it was proposed, on the one hand, to use nickel-plated rollers (Bayer), and on the other to add bisulphite (Cassella) to the printing colour.

Since then, special marks of these dyes have been introduced, which enable printing to be done, without difficulty, by the aid of hydrosulphite and lye, glycerine being added as a hygroscopic, and kaolin to prevent the impression from running. After printing, the goods are well steamed in a moist atmosphere in the Mather-Platt for 3 to 6 minutes, this being repeated and followed by washing and soaping. For some sulphur dyes the fabric must be soured in a bath of sulphuric acid and copper sulphate previous to washing (10 grammes of sulphuric acid and 2 grammes of copper sulphate per litre, at 50° C.).

The use of strongly alkaline printing colour enables discharge effects to be obtained with the sulphur dyes, *e.g.* on Turkey-red. Discharging the sulphur dyes themselves (oxidation) can mostly only be effected with light shades or on very thick fabrics, though certain of them, such as melanogene blue, discharge as easily as indigo and can therefore also be used for bottoming indigo dyeings.

Employment of the Vat Dye-Stuffs.

In addition to indigo, the vat dye-stuffs include: thioindigo red, thioindigo scarlet R, indophenol blue, indanthrene and several new anthraquinone dye-stuffs.

The method of direct printing with indigo formerly employed was the Schlieper-Baum glucose method, especially in producing fast red and blue styles by printing over Turkey-red.

The *modus operandi* is as follows: The fabric is first impregnated with a solution of grape sugar by padding, and then well dried. The printing colour consists of a thickened mixture of finely ground indigo paste and concentrated caustic soda, and the main point to be watched in its preparation is to prevent the mixture heating. The pressure applied in printing should be slight, in order to prevent the colour being forced too deeply into the fabric. The goods are then dried in a hot-air chamber to prevent the conversion of the sodium hydroxide into sodium carbonate—which would have a reducing action in the subsequent operations—and then steamed in a special chamber, where they are exposed for a few seconds to steam that is free from air.

If, however, hot dry steam (above 100° C.) be used, the steaming may be prolonged, and in this way the use of indigo can be combined with that of steam colours (Kalle). Steaming effects the actual fixation of the colour by reducing the indigo to indigo white, the fabric being then quickly washed—preferably opened out—with plenty of water which carries away the soda lye and re-oxidises the indigo white to blue.

The propiolic acid method of printing was only tried for a short time and on a small scale.

A more important method is that in which Kalle's "indigo salt" is used, the mark T in particular being suitable for delicate pale blue patterns. By means of a new method by the same makers, indigo salt can also be printed along with caustic soda, the colour being developed by steaming in the absence of air.

The Höchst method is also a good one, indigo paste, together with hydrosulphite and lye, being printed, and developed by hot (above 100° C.) steam free from air, in a special Mather-Platt.

The method is also suitable for producing the fast red-and-blue style.

Thioindigo red (Kalle), the first red vat dye-stuff, is well adapted for calico printing. The dye-stuff is printed along with caustic soda (hydrosulphite being added for dark shades), dried, and steamed at 106° to 108° C., the resulting leuco compound being developed, in the case of light shades, by washing with water, and, for dark shades, by entering in an acidified lukewarm bath of bichromate.

Owing to its great fastness and the method of fixation which enables it to be used along with indigo and sulphur dyes, thioindigo red is extremely valuable in calico-printing.

Indigophenol blue gives fast tones, very similar to indigo, when printed, though unfortunately it is very sensitive to steaming, and therefore cannot be combined with steam colours. Nevertheless a short steaming is indispensable for the fixing of the dye, despite the dulling effect thereby produced; and, indeed, the longer the steaming the faster the colour to washing and soaping.

To prepare the printing colour, the indigophenol is boiled with acetic acid, wheat starch, and tragacanth mucilage, and then mixed cold with a fivefold quantity of 20° B. tin acetate, with which it is left to stand for some time in order to effect the reduction to indigophenol white. After printing, the goods are left in the warm oxidising chamber for about thirty-six hours, then passed through ammonia vapour, to neutralise the acid in the printing colour, followed by a passage through the Mather-Platt, and by steaming in an enclosed chamber for a half to one hour, under low pressure. A pan filled with ammonia is placed on the floor of the steaming chamber. Finally, the goods are washed—also treated with potassium bichromate, if necessary—and hot soaped.

The indanthrene dye-stuffs can be fixed on cotton, like indigo, by the Höchst method with hydrosulphite and lye. The older method, in which the dye was printed along with tin salt and ferrous sulphate, and developed by passing through hot lye (containing a little manganese dioxide), has the disadvantage that the colour is liable to run.

Employment of the Acid Dye-Stuffs.

The acid dye-stuffs which are unsuitable either for the dyeing or printing of cotton, are very seldom used in calico-printing; actually, only for the so-called "Lucca" goods. The colours are fixed in the same way as in the case of the basic dyes for the same purpose. The dyes chiefly used are coralline, a few ponceaus, alkali blue, water blue, etc.

Latterly it has been found that the eosines can be fixed on cotton by the aid of chromium acetate, after the manner of the mordant dyes.

For the production of various tints in calico-printing, use is made of the above-named dyes, either separately or in combination; for instance, yellow and blue for green; the first point to be borne in mind being whether, in the case of designs in several colours, certain dyes are suitable for conjoint use as regards their behaviour in printing and during the requisite after-treatment. Thus, for instance, one cannot use in combination two colours one of which will not stand the prolonged steaming which is absolutely necessary for developing the other. Moreover, the best manner of producing a given article must be decided upon each individual case. For example, if the article in view is in a design of several colours on a dark ground, it will be necessary to consider whether the small coloured portions can best be produced by discharging or reserving the dark ground or whether it would not be preferable to print all the colours direct. The decisive factors in such cases are: the fastness and beauty of the resulting print, the relative practicability of the methods contemplated, and most of all, the cost.

Treatment of the Goods when Printed.

After printing, the goods are passed through a whole series of operations, comprising hanging in the oxidation chamber, putting through the Mather-Platt, steaming, the tartar emetic bath, the chalk bath, chroming, washing and soaping, malting, dung and malt baths, bran bath, chemicking (chloring), and dressing.

Leaving out of the question the last process of all, which will be dealt with separately later on, the object of the series of after-treatments is threefold: (1) fixing the colour; (2) purifying and enlivening the colours; (3) cleansing any white that may be present.

In most cases the goods are not fixed at all in the printing process, and could be completely washed off the fabric; consequently, the most important operation of these complementary processes is that of steaming, which effects the fixation of the colour, and, in the case of mordant dyes, develops and fixes the colour lake. The vat dyes and developing dyes alone do not require steaming. The oxidation chamber, and Mather-Platt treatments are preparatory to the steaming process, whilst the tartar emetic and chalk baths, and chroming, serve to complete the fixation of the colour in some cases. All the other operations are performed with the object of removing the thickening materials—since these dull the colours—to cleanse and brighten the colour, and also thoroughly clean the white from any stains arising from the imperfect action of the scraper in the printing press.

The passage through the oxidation chamber and the Mather-Platt are chiefly designed for the elimination of the excess of volatile acids contained in the printing colour. If strongly acid printing colours were immediately exposed to steaming, the liberated acid vapours might injure the colour as well as the goods. Hence it is necessary to pass goods that have, for example, been printed with sulphocyanides (alizarine red with aluminium sulphocyanide) two or three times through the Mather-Platt, or leave them two days in the warm oxidation chamber before steaming. At the same time these two operations also assist in the gradual formation of the colour lake, a consideration not devoid of importance. The goods are hung on rods in the oxidation chamber for about forty-eight hours (the hygrometer registering about 32° to 36°) during which time they are turned once, so that the parts at the top take up a position at the bottom, and *vice versa.* Frequently, however, the oxidation chamber is used merely for drying damp goods.

Nowadays many calico printers have abandoned the oxidation chamber entirely, in favour of the Mather-Platt, which serves the same purpose, especially when only a short steaming is required. The goods are usually fed through the machine at such a speed that every portion is exposed therein for a minute.

Steaming.—The piece to be steamed is backed with a layer of raw cotton, the object of which is to prevent stains arising from drops of condensed water, and is wound upon a collapsible frame, from which it is then removed—by holding the frame—and hung on a rod mounted on a carriage and caused to rotate by means of an attached cog-wheel. A whole series of pieces are hung in this way on the said carriage, which is then run along a track and introduced into the steaming chamber (Fig. 41).

This chamber may be cylindrical or quadrangular, and is fitted at the bottom with steam admission pipes—perforated with orifices directed downwards—and a pipe for drawing off the water, a horizontal partition being provided near the top of the chamber in order to prevent the dripping of condensed moisture. The apparatus must be warmed up before the goods are introduced, since otherwise the excessive condensation of steam might cause the colours to run. With this object the waste-pipe is opened to run off the condensed water, after which steam is turned on, and, as soon as all the water is drawn off,

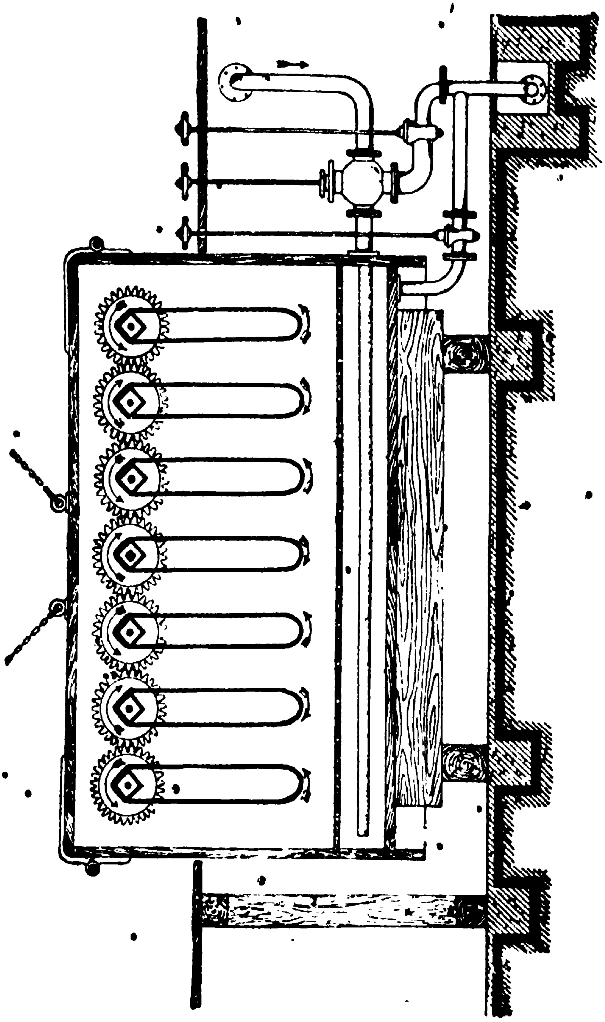

Fig. 41.

the pipe is shut and the pressure of steam is raised to about half an atmosphere. At the end of about ten minutes the steam and water are allowed to escape, the door is opened, and the goods entered, whereupon the door is shut and steam turned on, without pressure for the first few minutes, after which the effluents are closed and steaming continued for a half to two and a half hours, either without pressure or under a pressure of about half an atmosphere, the water of condensation being run off from time to time. Finally, steam is shut off, the doors opened, the carriage drawn out, and another carriage, loaded with goods, introduced in its place, the steaming being then resumed as before. The steamed goods are unwound, separated from the cotton backing, and passed on for further treatment.

The duration of the steaming process and the pressure employed therein depend on the dye. Albumin dyes are steamed for a half to three-quarters of an hour; tannin dyes for an hour to an hour and a half; mordant dyes for one and a half to two hours. When several different colours are printed on the same piece, the duration of steaming is regulated by the colour that needs to be steamed longest.

Latterly the above method of steaming has been superseded in many establishments by a continuous process, the goods being passed over a series of guide rollers in a chamber filled with steam.

The **tartar emetic bath** is applied only to printings made with tannin dyes, the object being to fix them in a thorough manner by the formation of antimony tannate. The operation is performed in roller becks, through which the goods are passed at such a rate that each part only remains in the vessel one minute. The first bath contains about 3 parts by weight of tartar emetic and 13 to 15 parts of chalk per 1000 of water, the proportions varying according to the size of the pattern, and, in some cases, amounting to 20 parts and more of tartar emetic. The second bath contains 1½ parts of tartar emetic and the same quantity of chalk. The bath temperature is about 70° C. The object of the chalk is to neutralise the potassium bitartrate produced in the bath, the use of other, soluble, alkalis being inadvisable owing to the risk of injuring the colour.

In order to prevent the dulling of delicate colours by the more or less highly coloured bath liquor, the serial order in which the pieces are entered is determined by the sensitivity of the colours; those found by experience to be most liable to contamination by the bath being put through last.

For the same reason the goods are entered face downwards. After the passage of a certain number of pieces, the bath is recuperated by adding more tartar emetic and chalk. Old and foul baths are either run off or else boiled up along with chalk, left to settle, and the clear liquid used over again.

The **chalk bath** is used for goods printed with mordanted colours, and serves to neutralise the residual acid and thus complete the fixation of the colour lake. Just as in the tartar emetic bath, the goods are passed through two roller becks, charged with 1 per cent. of chalk, at a temperature of about 80° to 90° C., and then through a similar vessel containing clean water. The time of immersion in the bath is about one minute, and the bath is replenished after each piece. Goods that contain tannin dyes in addition to mordant dyes do not require to be put through the chalk bath, the excess of chalk always present in the tartar emetic bath being sufficient for the purpose.

Chroming is applied to secure better fixation of some colours by oxidation and the formation of a lake. The treatment is applied either cold or hot, and the method of performance varies in different establishments. One point to be borne in mind is that some dyes (*e.g.* alizarine red) may sustain alteration by the partial formation of a chrome lake, and in such case a cold or lukewarm chroming is best. The goods are passed through two roller becks, charged with a 4 per cent. solution of potassium monochromate, though in some instances the first bath alone consists of chromate, the second being merely water, which is frequently renewed. Between the two vats the goods are subjected to moderate pressure by a pair of squeezing rollers. Some articles are treated with chromate in just the same way as in steam chemicking (see later). In chroming goods containing alkaline dyes, the bath receives an addition of a little sal-ammoniac (1 to 2 parts per mil.), the influence of the alkali on the other colours present being diminished by the formation of ammonia or ammonium carbonate.

The chief purpose of washing is to remove the thickening materials present in the printing colour, and the work is performed in machines of different construction, according to the resisting power of the colour. The round washer, similar to that illustrated in Fig. 17, except that the upper roller is here replaced by a folding polygonal reel, is generally used; or the aforesaid vat can be employed, in which case the effect is increased by a beating roller mounted on one side. Goods that are very susceptible to the influence of washing are either left unwashed or washed without rubbing. For this purpose, full-width washing machines have been constructed in which the goods are passed through a series of roller becks fitted in places with a number of beaters; or the goods are made to circulate under water, without rubbing or coming up to the surface. To prevent the goods being dirtied by loosened particles of dye, it has latterly been proposed to add certain metallic oxides (zinc oxide, antimony oxide) to the washing water.

Soaping is chiefly resorted to in order to cleanse the white portions of the goods and to revivify the colours, an addition of a little sodium stannate being often given to the soap bath for this latter purpose, especially in the case of alizarine red.

Marseilles soap is used, and should not contain any free alkali. It is inadvisable to introduce the soap in a solid state into the bath, owing to the risk of spotting the goods by the adherence of soapy particles. A solution of soap is therefore prepared beforehand, and a definite quantity is run into the bath for use, the amount depending on the number of pieces and nature of the dye to be treated, the usual strength being 3 to 5 parts of soap per mil. of bath liquor.

Mostly the goods are soaped in band form for about half an hour to an hour at a temperature of 60° to 70° C. Soaping considerably increases the brightness of alizarine red and alizarine rose, and in this case the goods are boiled in the soap bath for one to two hours; in fact, occasionally, when heavy patterns of alizarine red are in question, they are soaped twice over, or once under pressure in a copper retort. Tannin colours, not being so resistent, are oftentimes soaped only a quarter to half an hour at medium temperature. Should the goods have a considerable surface of white, it is advisable to soap in a full-width machine.

The **thickening materials may be eliminated** from the printed goods in an innocuous manner by treating them with a decoction of malt, this being especially suitable for starch thickenings on account of the solvent action of malt thereon. Malt may also be replaced by diastafor, a product manufactured by the Diamalt-gesellschaft, Munich.

A still better plan is to use a bath of cow-dung and malt, the latter removing the thickening, whilst the decoction of cow-dung cleanses the white with less harm to the colour than by soaping. This method is applied to multi-coloured upholstery goods after a slight soaping, as many as five dunging baths being used. They are charged with 5 parts of cow-dung and 6 parts of malt (both boiled in water) per mil., and used at a temperature of 35° C. After the first two baths the goods are washed.

Some articles—logwood black in particular—are cleansed with bran, by treating them in a hot decoction of this substance once or twice over. The solution is prepared by boiling the bagged bran in water, at the rate of 11 to 12 parts per mil.

Chemicking, or chloring, serves to bleach the white portions of the fabric that have been left somewhat muddy looking by the washing and soaping processes. It is a very important, and in some cases indispensable, operation, since a perfect white is one of the best qualities of printed goods. There are two methods of application—steaming and the dry process. In the former case the goods are passed through a trough containing bleaching powder solution, squeezed between rollers, and led into a small wooden steaming chest, fitted with guide rollers and a false bottom, under which is a steam-pipe. On issuing from this chest, the goods are washed by a flushing jet and also by passing through a roller beck filled with water.

In the other method the goods are passed, printed side downward, through a pair of rollers, the under one of which is covered with flannel, and revolves in a solution of bleaching-powder. They are then led over drying cylinders.

The best strength of bleaching powder solution and the method of application depend entirely on the resisting power of the dyes. Usually the density of the solution is only a few tenths of a degree B., and it is frequently preferable in the case of very sensitive colours to apply a weak solution twice over than to use a stronger one once.

Frequently the chemicking is combined with blueing, a suffusion of ultramarine being added to the bleach solution, in which event the trough is fitted with a horizontal stirrer in order to prevent the ultramarine from settling to the bottom.

No generally applicable rules can be laid down for these various operations, and experience alone must decide which of them is suited to the needs of any particular case, and how they shall be carried out, in order to produce a beautiful white on the printed goods without injury to the colour. Mordant dyes are treated in the oxidisation chamber—the Mather-Platt—steamed, chalked, washed, soaped, and, if necessary, chemicked. Tannin dyes are put through the Mather-Platt, then steamed, entered in a tartar emetic bath, washed and soaped with care, and finally chemicked (usually by the dry method). Albumin colours are washed with the greatest possible care after steaming; acid dyes, on the other hand, must not be washed at all. For the most part, these printed goods are prepared by the aid of several very different dyes, and in such event the treatment is governed by the most sensitive of these.

Even one and the same article cannot always be treated in exactly the same manner, consequently the progress of each of the prescribed cleansing operations must be watched in every case, and an attempt made to correct any defects by employing some operation not usually practised, or by repeating one or other of the operations already performed.

Some colours that have suffered during the after-treatment can oftentimes be revivified by treatment with Turkey-red oil.

2. Combined Printing and Dyeing.

A second method of producing printed fabrics consists in first printing with one or more mordants and then dyeing with mordant dyes after fixing. Strictly speaking, the articles produced by discharged style or reserve style printing also belong to this category, inasmuch as they too result from a combination of printing and dyeing; nevertheless, the method of working is so different that a separate description is necessary.

The principal consideration in the production of combined effects being the retention of purity in the white portions of the fabric, the operation of oiling previous to dyeing must be omitted, because the oil has a fixing action on many of the dyes.

The suitably thickened mordants must be coloured in order to render the printed impression visible, for which purpose they are mixed with a dye that will easily wash out afterwards, *e.g.* a ponceau. The mixture generally contains an excess of acetic acid. After printing, the mordants are fixed, in the manner described in the section on mordants, and then dyed (see Dyeing with Mordant Dyes) along with an addition of size (4 oz. of gelatine per piece of about sixty yards), which prevents the staining of the white. The quantity of dye used depends on the area of the pattern. Red, Bordeaux, violet, brown, and black are chiefly produced in this way. The mordant used for red consists of aluminium acetate mixed with a little tin salt, yellow-tinge alizarine and size being employed for dyeing out. The stuff is then washed, oiled, steamed, soaped with an addition of sodium stannate, washed, soaped again, washed, and dried in the oxidation chamber. In this case the white must be cleansed by washing and soaping only, since these articles are not chemicked.

Small patterns in alizarine red are also sometimes produced in the same way, notwithstanding the difficulty of cleansing the white. This is done because alizarine red always comes out faster and brighter when dyed than when printed.

The other colours are generally produced in the following manner: Bordeaux, with aluminium acetate as mordant, and alizarine (bluish tinge), rubine and size as the dye; brown, with aluminium pyrolignite and iron pyrolignite as mordants, followed by dyeing with alizarine and quercitron, under addition of sumach, chalk, and size; violet, with iron pyrolignite as mordant, dyed with alizarine (bluish) and methyl violet, plus size; black, with iron pyrolignite, aluminium pyrolignite and zinc nitrate as mordants, dyed with logwood, quercitron, sumach, and size.

"In all these cases, except red, the goods must be chemicked, generally by a double dry chemicking, in order to properly cleanse the white. Black (mourning) goods are mostly treated with bran twice over. Of late years this method has largely gone out of use; but certain articles are now produced by dyeing over a printing of chrome mordant.

3. Discharge Style Printing.

White or coloured effects may be produced by discharging; in the former case, the task is merely the destruction or solution of the mordant, fixing agent, or the dye itself; in the other, the following alternative is open: (1) The discharge is printed along with a dye, towards which it is inert, and which is afterwards fixed on the fabric; (2) a mordant is printed along with the discharge, and the colour is produced by a subsequent dyeing.

Colourless discharges must be tinted before use. Some discharges contain such a large proportion of salts that they must be printed warm in order to prevent crystallisation.

The various methods of discharging may be arranged in three classes:—

1. Discharging the mordant.
2. Discharging the tannin-antimony fixing agent.
3. Discharging the dye-stuff.

1. *Discharging the Mordant.*

The unoiled fabric is padded with a solution of alumina or iron mordant and then dried in the cold, to prevent the discharging being impeded by a premature fixing of the mordant.

The discharge is then printed, the goods being afterwards passed once or twice through the Mather Platt—after a small sample has been dyed out in order to see how the discharge acts—dunged, washed, and dyed. In this process great care is necessary to guard against setting-off on the part of the discharge, and for this reason the goods must not be laid one upon another until thoroughly dry.

The discharge reagents consist of organic acids; and as oxalic and tartaric acid salts are sparingly soluble, ammonium citrate is generally used. The presence, however, of large amounts of free citric acid causes the discharge to run. In discharging alumina-iron mordants or weak iron mordants, an addition of sodium bisulphate is made to the discharge; concentrated iron mordants are discharged with citric acid and tin salt. Latterly, however, the practice of discharging alumina and iron mordants has been abandoned owing to the unreliable character of the operation.

The modern chrome discharge style is produced in a somewhat different manner. The goods are padded with chromium bisulphite, dried, printed with a discharge consisting of sodium chlorate and potassium bromate, steamed for over an hour, chalked, and dyed.

Coloured discharges can be produced on alumina mordants by means of tannin dyes in various ways. For example, the unoiled stuff is first mordanted and fixed, and then printed over with a thickened mixture of a tannin dye, with tannin and ammonium citrate. It is then steamed, entered in a tartar emetic bath, washed, and dyed with alizarine (for red) in association with Turkey-red oil and size. Only a few basic dyes are, however, suitable for this purpose, *e.g.* thioflavine T, Nile blue, and brilliant green.

2. *Discharging Antimony Tannate.*

The fabric is tannined, fixed with tartar emetic, and then printed with strong caustic soda thickened with roasted starch (containing 50 per cent. of 42° B. soda) and qualified with a little turpentine to prevent frothing. It is next dried, passed twice through the Mather-Platt—which should be charged with dry steam—washed several times, and then dyed with a basic dye, the white being afterwards cleansed by washing, slight soaping, and chemicking.

The method is modified by the Mühlheim Farbwerke as follows: The fabric is tannined and fixed at 65° C. in a tartar emetic bath containing chalk and common salt. It is then printed with a mixture of lye, bisulphite and grape sugar, steamed, and finally treated in a bath of size and sal-ammoniac at 35° C.

The tannin discharge style is now largely superseded by the fast oxazines and sulphur dyes, which are easily discharged by oxidising agents; and its use is really confined to dark navy blue, produced with new methylene blue and fast blue.

3. *Discharging the Finished Dye.*

Discharging Vat Blue.—Indigo discharge style is a very important branch of calico-printing, and enables finer details to be produced than is possible by reserve printing.

Three different discharges may be used for vat blue: (1) chromate discharge; (2) chlorate discharge; (3) alkaline discharge.

The chromate discharge is the most important, and the one most in use for colour discharge styles. For the production of a white discharge the fabric is printed with a solution of potassium bichromate thickened with starch -the quantity of bichromate depending on the depth of the blue to be discharged —dried, passed through the discharge bath, and well washed. The discharge bath, an aqueous solution of sulphuric and oxalic acids, is contained in a small vat through which the fabric is passed quickly by means of guide rollers. The working conditions are capable of considerable variation, the fabric being passed, for example, through a bath at a temperature of 45° to 50° C., containing 4 per cent. of oxalic acid and 5 per cent. of sulphuric acid, at such a rate that the time of exposure is a half to one minute. After leaving this bath, the fabric is washed under a jet and by passing through a roller beck filled with water.

Without oxalic acid a good discharge cannot be obtained in practice. This acid, as the author has discovered, acts essentially as a catalyst, since the rapidity with which discharging proceeds is in direct relation to the amount of oxalic acid used. To economise the acid attempts have been made to use it in the discharge colour instead of in the bath, by adding calcium oxalate to the colour and using sulphuric acid alone in the bath. Good results, however, are only obtained in the case of light shades, an unavoidable defect of the method being that, with dark shades, the fabric is corroded at the discharged parts of the design.

In discharging pale blue, or with coloured discharges, this defect disappears, the discharges used being weaker. The colours chiefly employed are chrome yellow and orange chrome (in paste form), vermilion, chrome green, and various ochres. They are thickened with albumin for printing, this substance then coagulating in the discharge bath and exerting a fixing action on the dyes. In this case neutral potassium chromate must be used as the discharge, since the acid salt coagulates the albumin. Vermilion is the least suitable of all the above-named pigments because of its high price and the readiness with which it rubs off, this tendency varying inversely in proportion to the amount of chromate used for discharging. It is now frequently used in admixture with insoluble red azo dyes.

For pale blue discharge a discharging solution is used that is too weak to entirely decolorise the indigo, but as the resulting colour is too dull to be of any practical value, a little Berlin-blue is added to the discharging agent, or the goods are passed through pure blue. Finally, the colour may be enlivened by the application of a blue dye such as pure blue, methylene blue, etc., in the dressing.

Of late years other oxidising agents, such as sodium chlorate and potassium ferricyanide, have come into use. The oldest of these is aluminium chlorate, which was originally employed for producing discharge red with alizarine, but is now also used for white, in small patterns, in steam printing. Vat blue can be discharged white by the prussiate method, in which the fabric is printed with a mixture of sodium chlorate (bromate for dark shades), potassium ferricyanide (red prussiate), and sodium stannate, the reaction (the exact nature of which has not been ascertained) being effected by steaming. Persulphate, too, is used for white discharges; and both these agents are superior to the chromate method inasmuch as they do not corrode the fabric nearly so much.

Potassium ferricyanide forms an admirable discharge for indigo in presence of a strong alkali; the method is, however, confined to the production of a bright rose-red with rhodamine, in which case all the other colours that may be present are also produced as alkaline discharge colours. The colours are printed in association with potassium ferricyanide, then dried, and passed through a strong solution of caustic soda.

Whilst vat blue can be discharged with reducing agents, such as tin salt or the new hydrosulphite preparations, the method offers no advantage over others.

For producing red discharge effects on vat blue—the popular red and blue style—alizarine is the chief dye-stuff used. The vatted blue fabric is printed with a discharge of aluminium chlorate, sodium bromate, copper sulphide, and a little potassium iodide, and then steamed and dyed out with alizarine. Para red is obtained as a discharge red on vat blue by printing the naphtholised vatted fabric with the discharge colour, any oxidising discharge that does not attack the para red being suitable.

The discharge of indigo blue with direct dyes has been proposed by the Farbenfabriken Fr. Bayer & Co. The vatted fabric is printed with a suitable dye (chrysophenine, brilliant geranine, etc.), mixed with potassium ferricyanide and magnesium carbonate (as the alkali), and then gently steamed for a quarter of an hour.

Thioindigo red can be reduced more satisfactorily discharged with reducing agents than with oxidisers. The best method, according to Luck, is to print with hydrosulphite and lye, steam 5 to 10 minutes at 108° C., and pass the fabric in succession through acid, boiling water, and lye, followed by washing and drying.

Nowadays, the sulphur dyes are also used for discharge printing, and can be satisfactorily discharged by oxidising agents, *e.g.* a mixture of sodium chlorate, aluminium chlorate, and ferricyanide. The fabric is, however, corroded, and the results lack uniformity. The important factor is proper steaming. This method is of particular importance for blacks (as a substitute for aniline black).

Turkey-Red Discharge Style.—There are two methods for the discharge of Turkey-red—the "*cuve décolorante*" (decolorising vat), introduced by D. Koechlin, and the caustic soda discharge.

In the first-named and older method, the discharge is effected by hypochlorous acid, the dyed goods being printed with a solution of tartaric acid thickened with dextrin, then dried and passed through a roller beck containing a solution of bleaching powder and quicklime. The lime renders the solution alkaline and thus nullifies the action of the bleaching powder on the unprinted portions of the goods. The decolorising bath must be tested in advance in order to ascertain whether it has been set in a proper manner for securing the end in view. It should not be too alkaline, or the Berlin-blue here used for the blue discharge will be attacked. On issuing from the bath the goods must be squeezed and at once immersed in water.

For yellow, use is made of a mixture of tartaric acid, citric acid, lead acetate, and a little nitric acid, with which the goods are printed; they are dyed out with lukewarm potassium bichromate after passing through the bleaching powder bath. The lime of the bleaching bath precipitates lead hydroxide on the printed impression, which oxide is converted into chrome yellow in the potassium bichromate treatment. To complete the process, the goods are finally entered in dilute hydrochloric acid and then washed.

For blue, the fabric is printed with a mixture of tartaric acid, oxalic acid, potassium ferrocyanide, and ferrous sulphate. The oxidising action of the bleach bath not only discharges the Turkey-red, but also develops the Berlin-blue.

Green is produced by mixing the discharges for red and blue, and then treating in the same way as for yellow.

At the present time the decolorising method is practically abandoned, the work being of a too delicate character. Difficulties arise in connection with the proper setting of the bleach bath and with the printing of the colours, which are strongly acid and loaded with pipeclay. The printing is performed on the Perrotine press.

In the method now preferred, the colour lake is dissolved by printing it over with a highly concentrated solution of caustic soda, followed by steaming. In this case, as the ordinary Turkey-red, produced by alizarine, is too difficult to discharge, the goods are mordanted with sodium aluminate and dyed with flavopurpurine anthrapurpurine. For yellow, the fabric is printed with sodium plumbate, and dyed with potassium chromate. Black is produced with alkaline black; blue, with indigo by the Schlieper and Baum method—printing on the goods prepared with grape sugar. The after-treatment is as follows: The goods are exposed to damp steam for one to two minutes, then hung for a day in the warm, washed, entered in 6° B. sulphuric acid, washed, dyed with 45° B. potassium monochromate, washed, soaped at 45° C., entered in 2° B. sulphuric acid, washed, passed through a bath of boiling bichromate, and washed again. Blue discharge effects on Turkey-red can be obtained in a simpler manner with indanthrene and hydrosulphite.

The **chrome discharge style** has latterly attained considerable practical importance, but is only applicable to soluble dye-stuffs. The goods are padded, for example, with alizarine blue S and a chrome mordant, dried, printed with the discharge, and steamed. The discharge used consists of potassium ferrocyanide and an alkali, or of a prussiate discharge.

For the illumination of the article, and also for parti-coloured discharges, the direct dyes have been recommended; but only a few of them (*e.g.* chloramine yellow) are able to withstand the discharge reagents employed.

The discharge of finished tannin dyeings never attained any great importance. In order to produce this article, if desired, tannin-antimonate lake is discharged before dyeing. The finished dyeings can be discharged by printing with strong caustic soda and glucose, or with a prussiate discharge. Pyronine, etc., can be discharged really well.

Discharging Manganese Bistre.—The goods are printed with a discharge consisting of tin salt and citric acid, and then hung cold until the discharge is complete, after which they are passed through a cold chalk bath and washed. For coloured discharges use is made of basic dyes—malachite green and methylene blue—as well as mineral pigments and colour lakes.

The discharging of Ice Colours in the finished state presents—owing to their insolubility—considerable difficulties, which have only been completely overcome within recent years. The discovery of such a method was highly desirable because, in contrast to the easier reserve process, it offers the advantage of enabling the fabrics intended for discharging to be dyed for stock.

The first pure white discharges on para red were obtained by H. Schmid of the Hochst Farbwerke with "Azorongeant," a mixture of tin salt, ammonium citrate and acetine; and by Kalle & Co. with a (somewhat unstable) mixture of aluminium powder and potassium sulphite. Alkaline discharges, with stannous oxide, or with glucose and alkali, also give fair results. The first entirely satisfactory solution of the problem, however, was provided by the stable hydrosulphite preparations, such as hydrosulphite NF, though at first only for para red. With the exception of the mark *z* (zinc hydrosulphite), the hydrosulphites were not altogether satisfactory for white discharges on the more highly resistant *α*-naphthylamine Bordeaux; and the insolubility of this mark *z* gave rise to printing difficulties. Better results were obtained with the alkaline iron discharges (hydrosulphite and an alkaline iron solution) and the nitrate discharges (formaldehyde-sodium sulphoxalate, iron citrate, sodium nitrite and glycerine) of Baumann & Thesmar; until, finally, it was discovered that the hydrosulphites are capable of effectually discharging even naphthylamine Bordeaux when used along with a small amount of certain substances, especially dye-stuffs. These preparations give excellent discharges when the printed fabrics are treated with superheated steam. For coloured discharges on ice colours, the basic dye-stuffs, oxazines, sulphur dyes and indanthrene are used.

Nitroso blue can be discharged by printing on the padded colour with tin acetate or potassium sulphite, or with a mixture of potassium-sodium sulphite and sodium citrate, and then steaming.

Discharging Direct Dyes.—For this purpose stannous salts occupy first place. They are printed on the fabric, which is then put once or twice through the Mather-Platt. Tin salt by itself corrodes the fabric, and tin acetate gives imperfect results, for which reason a mixture of the two is used. Better results are obtained with tin rhodanate (Elb.) or tin ferrocyanide (Cassella), prepared in the printing colour itself by the reaction of tin salt and ammonium sulphocyanide (or ammonium ferrocyanide).

These tin discharges give a defective white, which turns yellow. At present hydrosulphite alone (which is free from this drawback) is used for white discharges on direct dyes, whilst the tin salts are better for coloured discharges.

The mixture of zinc dust and bisulphite, formerly used for white discharges, was very unpractical and has been abandoned.

For **coloured discharges**, use is made of basic dye-stuffs which are printed in association with tannin and the discharge preparation. After the printing, the goods are steamed for one hour under a pressure of half an atmosphere, then passed through cold 2° to 3° B. sulphuric acid, and finally well washed.

For coloured discharges, tin salt (stannous chloride) cannot be used alone, owing to its corrosive action on the fibre; and if neutralised with sodium acetate, does not discharge properly. For this reason a mixture of tin salt, tin acetate, and sodium acetate is employed, or the first two, along with a little citric acid and acetic acid. The dyes used for this style are basic dyes, and are printed on the goods in association with tannin and the discharge. After printing, the fabric is passed once or twice through the Mather-Platt, steamed with dry steam for a half to three-quarters of an hour, entered in a tartar emetic bath, and washed. Most of the basic dyes, however, are partially decomposed into their leuco-compounds by the discharge reagent during the steaming process, and, in order to remedy this, it is then necessary to pass the goods through a lukewarm solution of potassium chromate and dry on a hot drum.

For colour discharges with direct dyes it has been proposed to use certain mordant dyes, such as buckthorn berries, gallocyanine, cœruleine, etc., the dye being printed along with tin acetate and a chrome mordant.

The following direct dyes are very suitable for discharging: Diamine yellow, benzazurine, heliotrope, Congo-red, etc.

4. Reserve Style Printing.

This term is applied to the process whereby various substances, printed on the fabric, are employed to prevent either the absorption or development of the colours subsequently applied by padding or dyeing. Hence there is no difference in principle between discharging and some reserves which are known as discharge reserves.

The chief reserve style articles are those with vat blue, tannin dyes, alizarine rose, alizarine violet, ice colours, and aniline black.

Reserve printing under vat blue is perhaps the oldest division of this industry; at present it is mostly produced in the hand-press.

Use is made of a mixture of several substances, the reserving action of which is partly mechanical and partly chemical. The chief mechanical reserves are pipeclay and fatty bodies, which prevent the vat liquor from penetrating the underlying cloth. The chemical reserves consist of copper salts for the most part, these also preventing the fixation of the indigo on the printed places, inasmuch as the indigo blue is oxidised to indigo white if it penetrates into the reserve coating, and is therefore precipitated in merely a loosely adherent manner on the reserve.

After the reserve has been printed, the fabric is well dried, and is then dyed by short immersions in strong vat liquors, and finally soured and washed without friction. The continuous dyeing process cannot be used, since the friction of the guide rollers would dislodge the reserve. The foregoing method is applied to the production of white reserve patterns. For yellow, the reserve also contains lead acetate, and in this case the goods, after dyeing and souring, are passed through lime-water to neutralise the acid and treated in a warm bath of potassium bichromate at the rate of 11 oz. per piece of about sixty yards, whereby yellow lead chromate is formed on the printed parts. The same method is followed for green, except that the reserve is printed on a slightly blued ground instead of on white, so that the resulting chrome yellow combines with the underlying blue to form green.

For **thioindigo red,** in contrast to indigo, oxidation discharges are unsuitable. The fabric is printed with reserve solutions of mineral salts, then padded with the alkaline thioindigo red colour, and finally steamed. Reserve salts for this purpose are put on the market by Kalle & Co.

In reserving **indanthrene dye-stuffs,** use may be made of protective pulp, as in indigo printing, or else chemical reserves are employed, such as mixtures of hydrosulphite and metallic salts, or sodium chlorate and tartaric acid.

Sulphur dyes can be reserved by being printed over with mixtures containing salts of copper, zinc and lead, in addition to pipeclay.

Reserve with Tannin Dyes.—The method is performed as follows: The unoiled stuff is first printed with a reserve containing an antimony salt, and dried; the suitably thickened basic dye and tannin are next applied, well dried (otherwise the reserve will run), steamed under pressure for half an hour, entered in tartar emetic, washed with hot water, and finally soaped lukewarm.

The reserve should contain as much antimony salt as possible; and, as tartar emetic is too sparingly soluble in pure water, it must be mixed with about its own weight of common salt before dissolving. The more readily soluble potassium-antimony oxalate makes a good reserve when thickened with dextrin, without any admixture of common salt.

Reserves under Alizarine Rose and Violet.—For the production of these very handsome and important articles sodium citrate or tartaric acid is printed as a discharge reserve, dried, topped with the dye, and steamed. In the subsequent washing, the colour lake is thrown off from the reserved parts of the design on which it was unable to fix.

Reserves under Ice Colours.—Since the introduction of the stable hydrosulphite preparations, which enable ice colours to be discharged in a thoroughly satisfactory manner, the reserve processes, in which certain substances are printed over the naphtholised fabric before developing the colour in the diazo solution, have become of minor interest. The reserves used are either reducing substances such as tin salt or potassium sulphite, or else substances (tannin, naphthol, sulphonic acids, etc.), which combine with the subsequently applied diazo compounds to form a dye-stuff that can be easily washed out.

As in the discharge method, difficulty is found in obtaining good whites. Fine coloured effects are produced with basic dye-stuffs by the Rolffs method, in which the naphtholised fabric is printed with a mixture of dye solution and an excess of tannin (*i.e.* more than is needed to fix the dye-stuff), the fabric being then steamed and passed through the diazotising bath.

For the production of the red and blue article two different methods are employed. According to the process of the Höchst Farbwerke, the goods, prepared with naphthol, are printed with diazotised dianisidine and ammonium persulphate, dried, passed through diazotised p-nitraniline to which a little ammonium oxalate has been added, and finally washed and soaped in presence of ammonium oxalate. The diazotised nitraniline combines with the β-naphthol to form red, except in those places occupied by the dianisidine impression, since the excess of β-naphthol there has been destroyed by the ammonium persulphate. The addition of ammonium oxalate to the diazotised nitraniline is for the purpose of preventing the browning of the nitraniline red by the copper in the dianisidine printing colour.

In the second method for producing the same article (Tschudi & Co.'s patent, assigned to the Farbenfabriken Fr. Bayer & Co.) the procedure is reversed, the goods, prepared with naphthol, being printed with a mixture of diazotised p-nitraniline and aluminium sulphate, dried, and passed through diazotised dianisidine; the latter is reserved by the aluminium sulphate, and hence the development of the blue is confined to the unprinted portions of the fabric.

Reserves under Aniline Black.—This article is one of the most important in modern calico-printing. It is produced, by the aid of Prudhomme's black, by first padding the fabric with the solution of aniline ferrocyanide, then drying and printing with a reserve consisting of sodium acetate, soda, and bisulphite, the black being afterwards developed as in ordinary dyeing. Tin sulphocyanide can also be used as reserve. The process therefore rests on the circumstance that the aniline ferrocyanide black does not develop until steamed, and that this can be entirely prevented by the aid of alkaline reagents. Sodium aluminate or sulphocyanides can also be employed as reserve.

For the purpose of illumination, use is made of mineral pigments and basic dyes, the direct dyes being less suitable by reason of their inferior brightness. The mineral colours, as well as various colour lakes, are also fixed with albumin.

Coloured reserves are best obtained by the aid of basic dye-stuffs, various methods being practicable. One good way is to print with a mixture of dye-stuff solution and zinc oxide, the action of which is twofold: on the one hand, the zinc oxide combines with the hydrochloric acid of the aniline salt and prevents blackening; whilst on the other, the simultaneously formed zinc ferrocyanide fixes the basic dye-stuff. In addition to low cost, this method has the advantage that the reserve can be printed on before padding with the aniline black preparation. Its defect, on the other hand, is that the fixation of the dye-stuff is not particularly good.

Latterly, the Prudhomme article has been largely produced by means of diaminogen black, which can be discharged effectively by hydrosulphite.

Diphenyl black can be reserved with potassium sulphite.

5. Topping Printing.

In this method, goods that have already been printed and dried are put through the press again and topped with colour, either all over or in the form of a pattern. In the former event the colours must be in very pale tints, since otherwise the colour of the underlying pattern would undergo a too extensive alteration.

The colours used for complete topping are—alizarine rose, chiefly for the alizarine rose article; alizarine violet, for the corresponding violet article, white reserve being usual in both cases; further, various direct dyes—chloramine yellow, a few diamine yellows, chrysamine, chloramine brown, brilliant geranine, diamine pure blue, diamine violet, etc. For the most part these are applied along with the dressing, and not in the press.

A further application of the same process is when it is desired to dye fabric on the one side only, in which event the stuff is printed with a thickened mordant solution, fixed, and dyed.

The object served by topping a design is either the production of a mixed shade by the superposition of two dyes, or else the discharge of the topping colour on the parts already coloured. In the latter case the ground colour must contain an addition of a reserve for the topping colour.

Although the method enables the production of some very special effects, it is cumbrous and tedious, especially when several colours have to be applied. The ground and topping colours cannot be applied at the same time, since they would come together in a wet state, and thus produce a mixture of an unanticipated character, or else run. According to Casanova, however, this simplified method of the topping process becomes possible if an addition of turpentine be made to the printing colours.

Pile-printing is a method in which the contact between the fabric and printing roller is so slight that only the raised portions of the former receive the impression.

Opaline and metal-printing are also two special forms of calico-printing. The former consists in printing the fabric over with a white substance (mostly barium tungstate) which contrasts with the ground colour so as to produce a damask effect. Viscose, either alone or with zinc oxide or kaolin, is also used.

Metal-printing consists in applying a coating of lustrous bronze powder, silk-weave effects being very finely imitated. The colour may be fixed with albumin, ammonia-casein or varnish solutions. S. H. Sharp & Sons, Leeds, attained great success in this style of printing.

Wool-Printing.

Although very old, it is only of late that wool-printing has been practised to any great extent; but now large quantities of cloth, flannel, wool, muslins, and cashmeres are printed.

The material to be printed must be carefully cleansed. Fine goods and yarns are also first bleached, an operation now performed exclusively with hydrogen peroxide and bisulphite. (See Wool-Bleaching.)

At an early period it was observed by J. Mercer that in printing half-woollens the dye was very imperfectly taken up by the wool. This he attributed to the reducing action of the wool, probably in consequence of the liberation of the contained sulphur, in the form of sulphuretted hydrogen or sulphurous acid, by steaming. Consequently he recommended that the wool should be prepared by chemicking, a method that is still generally practised.

Most dyes show up much fuller on chemicked wool, though the operation must be performed with great care, or the wool will become yellow and rough. In the case of combed sliver especially, the chemicking must be very slight, since otherwise the spinning and fulling properties of the fibre will be affected. In this case it is better to chemick the wool insufficiently, and to add a little sodium chlorate, as oxidising agent, in preparing the printing colour from dyes that are sensitive to the action of reducing agents, *e.g.* azo dyes. Deep grounds cannot be obtained perfectly uniform unless the wool is chemicked, though for some dyes, particularly eosines (which have been largely superseded by rhodamines), no chemicking is necessary. This treatment tends to prevent shrinking.

A second method of preparing the wool consists in precipitating stannic acid on the fibre, a treatment that increases the brightness of most printing colours, and also fixes some of them (the eosines, for instance) better.

As in the production of multi-coloured articles the most divergent dye-stuffs are used, it is customary to employ both preparations in the case of finer goods. In such event the goods are damped and padded twice with a 3½° B. solution of sodium stannate, after which they are left covered up for some time, and then passed through 2° B. sulphuric acid, to fix the tannic acid, followed by immersion in a solution containing 4 per cent. by volume of 3° B. sodium hypochlorite and 0·43 per cent. of 66° B. sulphuric acid (this being less likely to yellow the wool than bleaching powder and hydrochloric acid). The chemicking bath must be kept replenished by a constant influx of a more concentrated solution, since otherwise the first portions of the goods would be more strongly chemicked than the rest.

Hand and cylinder presses are used for printing, as in the case of cottons; common and very wide goods are printed by hand, wool muslins and similar fine goods by the cylinder press. The cylinders must be deeply engraved, and a very elastic pressure secured by the use of thick soft blanket on the backing rollers. The printed goods should be dried very gently.

The dyes used in wool-printing are in general the same as for dyeing this fibre—chiefly acid dyes; and dextrin, British gum-arabic and various "soluble" gums (*e.g.* gomme Labiche) are used for thickening. Direct dyes are used with sodium phosphate for colours to stand washing; basic dyes for discharge colours. The printing colours are almost invariably prepared with an addition of an organic acid, chiefly acetic acid, though in some cases tartaric acid or oxalic acid is preferable. For light tints and dyes that equalise with difficulty, it is advisable to employ slightly ammoniacal printing colours. When the colours are required to remain slightly moist after drying, a little glycerine (5 to 8 oz. per gallon) should be added to the printing colour.

Printing is succeeded by steaming, which fixes the colour. The operation must in this instance be performed damp, since the majority of printing colours on wool do not develop properly under dry steaming; on the other hand, excessive moisture is injurious, since it makes the colours run. Consequently, in order to ensure correct results, the steaming must be effected in presence of a pre-determined and readily controllable quantity of moisture, a condition fulfilled by enveloping the goods in cotton cloths previously impregnated with a definite quantity of water (10 to 20 per cent. of their own weight) by padding or sprinkling. This weight can be ascertained by weighing these backing cloths before and after damping. Steaming is continued for an hour to an hour and a half, according to the dye, and mostly without pressure. A careful washing follows, in order to prevent the soiling of the white by the dye; finally, the stuff is slightly dressed with gum, glycerine, or starch.

Wool-printing is therefore a far easier operation, and one presenting fewer technical difficulties, than calico-printing; in fact, the now so popular discharge printing is the only difficult form. In this case the chief question is, which of the dyes are suitable for discharging, and which capable of properly resisting the action of the discharge reagents.

As in discharging the direct dyes on cotton, coloured discharges are here effected with tin salt, and white discharges with zinc dust and bisulphite; the hydrosulphites such as NFW and hyraldite W being also very successful.

Most of the azo dyes discharge well, though here, as in the direct dyes on cotton, there exist difficulties that have not yet been overcome.

The dyes best resisting the discharging action of tin salt, and therefore constituting the most suitable dyes for coloured discharge style, are—the majority of the basic dyes, the eosines, and the acid dyes of the triphenylmethane series, especially azocarmine, diamine yellow FF, thioflavine, quinoline yellow, new methylene blue, fast blue, lano-glaucine.

The discharge colours for white contain, in addition to hydrosulphite, zinc white and ultramarine or other blue dye to mask the yellow tinge of the fibre.

After printing, the fabric is left rolled up for some time in contact with the damp backing cloth, and then treated, without backing, in the Mather-Platt for some time with dry, hot steam. If the coloured discharge dyes reduced by the discharge do not reappear on exposure to the air, the goods are passed through a weak bichromate bath before rinsing. The beaming of the goods after steaming requires special care.

The new hydrosulphite preparations have been of great advantage in wool printing; and large quantities of black, dark blue, red and brown grounds are discharged white and green.

Discharge effects can also be produced on half woollen fabrics in just the same way.

Silk-Printing.

The same methods and printing colours are used for printing silk as in the case of wool, except that no preparation of the fabric is necessary, and that dry steaming is practised. After steaming, the goods are for the most part only carefully washed, the colours revivified as in dyeing, and given a slight dressing.

In this case also an important part is played by discharge printing with the same discharges; in contrast, however, to wool, a number of effects can be produced on silk by reserve printing (with fatty reserves) and dyeing.

Printing Yarns, Warps, and Combed Sliver.

The printing of yarns is a comparatively young industry, but one that is constantly increasing in importance on account of the possibility of producing a variety of patterns by weaving the partly coloured yarns. Formerly it was the practice to tie the yarn together and dye it at intervals of its length, and subsequently the hand-press was employed for this class of printing; but at present the work is done exclusively on printing frames of special construction.

For printing yarns, the machines of Donath, Dehaitre, etc., are used—those employed for warps being either such as enable the work to be done in the same way as with hand-presses (Morton, Kefer) or in which the material is printed on drums (Schmidt, Hofmann, Hallensleben).

The printing of combed sliver is termed "Vigoureux printing," and has latterly come very much to the front. The printed sliver is used for the production of mixtures, to which it imparts a very uniform appearance.

The composition and method of fixing the printing colours are, in the main, the same as in cloth-printing.

Successful attempts have also been made at imitating mixtures by printing piece-goods, a method which offers the advantage of dispensing with the necessity for keeping stocks of various yarns. H. Giesler (Molsheim) employs the following method: a small pattern design is printed in fast colours, the fuzzy effect being obtained either by gradual milling or by raising. L. Hirsch (Gera) prints a broken cross-hatched pattern, no after-treatment being required. Fancy threads are imitated by discharging or by printing with aluminium bronze powder.

A similar method is used by F. H. Schneider (Mylau).

CHAPTER VI.

DRESSING AND FINISHING.

THE operations of dressing and finishing comprise all the treatments employed to impart to the fabric the special feel and appearance likely to render it most attractive to the purchaser.

The number of methods employed in the finishing of fabrics is almost beyond count; they may, however, be all classed under two heads—

1. By impregnating the material with various substances;
2. By subjecting it to a small number of mechanical operations, which, however, are performed in very different modifications.

The finishing of fabrics almost entirely belongs to the domain of mechanical technology, its practical performance being only in a very few instances (such as calico-printing) the task of the the chemist. Nevertheless, a certain degree of acquaintance with this branch of the subject is necessary to the dyer's chemist, on the one hand, as supplementing his special knowledge, and, on the other, to enable him to detect many defects that may arise in the course of the various operations coming under the head of the finishing process, which he would otherwise be unable to do.

Finishing may in part precede dyeing, in which event the first part of the process will be the task of the dyer, whereas the remainder is frequently performed in special establishments —"the finisher's".

In the cotton industry the term finishing applies exclusively to the concluding stages of manufacture.

The complete description of this entire process in all its many ramifications can only be given in a work specially devoted to the subject; and the author will therefore confine himself in the following to the means employed in this stage of the manufacture.

The substances used in the finishing process are:—

1. Such as are intended to render the material hard and stiff. These comprise chiefly the various starches—wheat, potato, rice, and maize starch; also several starch derivatives, such as dextrin and apparatine; furthermore, gum, tragacanth, size, vegetable mucilage, decoctions of lichens and algæ, etc.

Of these materials the most frequently used are wheat starch, potato starch, and dextrin. The softest dressing is furnished by dextrin, next in order coming potato starch.

For dressings the strength in the case of starch rarely exceeds 90 parts per 1000 of water, whilst up to 300 parts of dextrin are used. In making the paste it should be noted that prolonged boiling hydrolyses starch and produces thinner dressings. Maize and rice starch in particular should not be boiled more than a few minutes. When very stiff dressings are required, glue is added.

There are various starch dressings on the market under the names: apparatine, crystalline, globeline, etc., prepared by cold gelatinisation, the starch (*e.g.* potato starch) being mixed to a milk with water and then stirred for several hours along with caustic soda lye, the excess of which is finally neutralised with acetic acid. These preparations are particularly suitable for delicate fabrics, and produce stiff dressings difficult to separate from the material.

The so-called "soluble-starches" are also largely used. These are prepared by boiling starch for a long time either with water only or with an addition of a salt (*e.g.* magnesium chloride), malt or other substances, the starch being more or less completely hydrolysed. Owing to the sugar present, they give soft dressings; and they are also suitable for woollens.

2. **Fatty substances,** such as tallow, stearin, paraffin, waxes, oils, Turkey-red oil, etc., to render the stuff soft and glossy.

The suitability of fatty substances depends on their melting-point. Monopole soap and "softening" (a palm oil soap) are largely used. The former is for soft dressings, and replaces fats (up to 20 parts per 1000) in thin dressings especially. It is also advisable for dressings high in saline matters or those that only penetrate the fabric with difficulty; and is very useful for silks, half-silks, and woollens.

"Softening" is used for producing a scroopy effect on cottons, the fabric being soaped and passed through a bath of acetic or lactic acid.

3. **Hyroscopic and softening materials,** to diminish the stiffness of starched goods, such as glycerine, magnesium chloride, zinc salts, ammonia salts, etc. Too much of these adjuncts must not be used, or the cloth will become wet and flaccid on exposure to damp air.

4. **Loading Ingredients.**—China clay (a fine white clay), kaolin, insoluble salts of lime and baryta, etc. Casein forms a useful bind.

5. **Colouring for the Dressing Preparations.**—Chief of these is ultramarine, which is so largely used in "blueing" cottons and linens, its object being to convert the yellowish tinge of the goods into a more or less pure white. In printed goods the selection of the correct shade of ultramarine is a matter of some moment, since here the degree of whiteness may vary. Some of the ingredients used in the dressing (*e.g.* China clay) absorb ultramarine, the shade of which is then modified accordingly.

Ultramarine is difficult to moisten with water, and should therefore be mixed to a paste with a little alcohol. Dressing preparations containing this colour should not be kept long or they may turn sour, to the detriment of the ultramarine, which is sensitive to acids. On this account the fabric should be free from acids (from the bleaching process, for example), since these decompose the ultramarine and leave the material yellow. To impart a strong blueing to any fabric, it is better to apply a weak ultramarine dressing two or three times over than to treat once with a stronger preparation.

Other colouring matters employed in dressing preparations are Berlin-blue, ochres, direct dyes, basic dyes, etc., either to impart a given shade of colour to a white or printed surface, or else to prevent the colours being dimmed by a superimposed white dressing.

6. **Metals or their sulphides,** in the state of fine powder, for the purpose of producing a metallic lustre. They are prepared by heating the metallic sulphides with fatty substances or by mixing different metal powders, and can be purchased ready for use. They are applied to the fabric by dusting or printing.

7. **Waterproofing** is effected by the application of fatty bodies, caoutchouc solution, salts of alumina or magnesia, etc., either together or separately. The most important process is the waterproofing with fatty acid compounds of alumina, which must be produced on the fibre (from aluminium acetate and soap).

8. **Fireproofing,** or at least non-inflammability, is secured by applying to the stuff a considerable quantity of various salts, such as borax, ammonium phosphate, salts of magnesia, silicates, tungstates, etc. The last-named salts, sodium tungstate in particular, are said to give the best results.

9. **Antiseptics for the Prevention of Mould.**—The majority of the means proposed for this purpose are no use, *e.g.* tannin, camphor, oxalic acid, boric acid, etc.; the most efficacious are zinc chloride, zinc sulphate, salicylic acid, and formic acid.

Dressing.

The dressing preparations are compounded with the assistance of the ingredients specified above. Sometimes they contain only a single ingredient, *e.g.* a starch, dextrin, gum, size, Turkey-red oil, etc., applied in the form of a solution or paste; mostly, however, several are employed together, *e.g.* wheat starch and potato starch, or starch and fat, or hygroscopic substances. The number of ingredients may amount to as many as ten, which are mixed together and boiled in the same class of pan as that already described for starch thickening; the product is passed through a strainer.

In most cases the finishing process is not completed by the application of the dressing preparation to the goods, a further mechanical treatment being required to impart the desired feel and appearance to the stuff.

Dressing preparations are confined almost exclusively to cottons and linens, the finishing of woollen and silk goods being usually effected without the aid of these preparations, and merely by mechanical treatment; and even where used at all on these latter goods these dressings are of very simple constitution. Solutions of gum, dextrin, or tragacanth are used for silks, and solutions of gum, size, vegetable mucilage, magnesium chloride, etc., for woollens.

The application of the dressing preparation is in nearly all cases made to the back of the fabric, and is performed in different ways, according as the quantity used is great or small. This method of working is particularly advantageous in the case of printed goods, since otherwise the printed colours would be dimmed by the dressing.

The simplest way is to pass the goods, face upwards, between a pair of rollers, the under one of which is covered with a layer of cotton and dips into a trough containing the dressing preparation (Fig. 42, *a*); the heavier the pressure applied to the rollers the smaller the quantity of dressing that will be left in the fabric, and the farther will it be forced into the material. Another way is to arrange below the pressure rollers a third, which dips into the dressing and distributes it on to the under roller of the pair (*b* in Fig. 42). For conveying still smaller quantities of dressing preparation onto the fabric, use is made of a stippled under roller, fitted with a scraper (*c* in Fig. 42). When the dressing is to be pressed as little as possible into the substance of the fabric, the arrangement shown in *d*, Fig. 42, is employed.

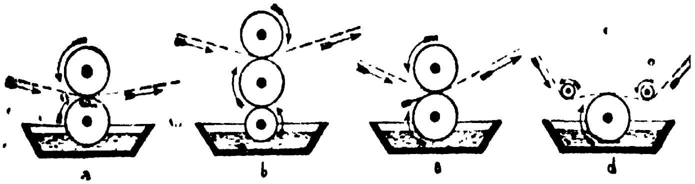

FIG. 42.

To apply the dressing equally to both sides, the stuff itself is passed through the preparation and is then squeezed between a pair of rollers. Where it is desired to force the dressing well into the fabric a pair of squeezing rollers are used, the larger lower one being of wood, whilst the upper roller, of metal, is run at a higher speed.

Where, as in the case of thin preparations containing ultramarine, there is a likelihood of the ingredients becoming separated, a stirring device is provided in the trough; the latter can also be heated in case the application of hot dressings is advisable.

Sometimes, in the case of woollen or silk goods, the dressing is applied with a sponge to the back of the stuff stretched taut in a frame.

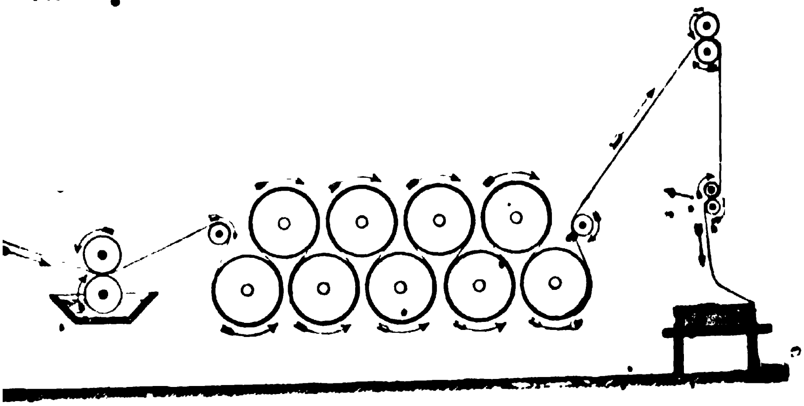

FIG. 43.

After applying the dressing, the next step is to dry it, for which purpose use is made of the cylinder drying machine (in the case of cottons and linens), *i.e.* a number of heated metal cylinders, generally arranged in two rows, as shown in Fig. 43.

When it is desired that only one side of the material should come into contact with the heated cylinders, those of the lower row are replaced by unheated wooden rollers. This class of drying machine is employed also for drying goods that have not been dressed. In some cases a single large drying cylinder is used, or the goods may be dried on frames (see below) or in the air (silks and woollens).

Frequently the necessity arises for straightening out the goods and stretching them out to their proper width. In such event the drying is effected on the stenting frame, of which there are several modifications. They may, however, all be divided into two main types—the circular frame, consisting of a large drying cylinder, fitted on both sides with adjustable stretchers, and the ordinary horizontal tentering frame, wherein the fabric is conducted over steam plates and hot pipes by means of two hooked endless chains. The stretching device can be adjusted to agree with the desired breadth of the fabric under treatment. There are also stationary tentering frames, in which the cloth is held on the stretch, without motion; these are chiefly used for light cotton fabrics, muslins, tarlatans, etc., and consist of wooden frames, the sides of which are movable, and are provided with clamps for holding the fabric. The latter, when treated with the dressing preparation, is secured in the frame, which is of the same length as the piece of cloth; it is then stretched to the desired extent, and left to dry in the frame. Similar frames are also used for woollens and silks. Sometimes the sides of the tentering frame are provided with an alternating reciprocal movement, so that the material can be kept moving to and fro whilst drying, in order to distribute the dressing preparation embedded between the individual threads of the fabric, and thus impart a greater uniformity of appearance to the whole.

In finishing cotton goods, the following operations are employed, in addition to those already mentioned: Damping, gassing, shearing, raising, calendering, mangling, beating, moiréing, stamping, folding, lapping, measuring, and pressing. Of these processes two are employed at a much earlier stage than the rest: gassing before bleaching, and shearing after bleaching is completed.

Shearing is performed in order to remove coarse irregularities, loose ends, naps, etc., and is an indispensable operation in the case of printed fabrics, since these irregularities would spoil the impression, by preventing the access of the colour to the underlying body of the fabric, and thus leaving white marks in the pattern on the subsequent removal of the loose ends and naps. Various forms of shearing machine are employed, the cutting being usually effected by a revolving cylinder, carrying a number of spiral steel blades, working against a fixed horizontal knife. The fabric is first passed over brushes which raise up the loose ends, fibres, etc., into position for removal by the cutting mechanism. Usually these machines are fitted with two sets of cutters and several brushes, to enable the stuff to be shorn on both sides.

After leaving the shearing machine, the pieces are opened

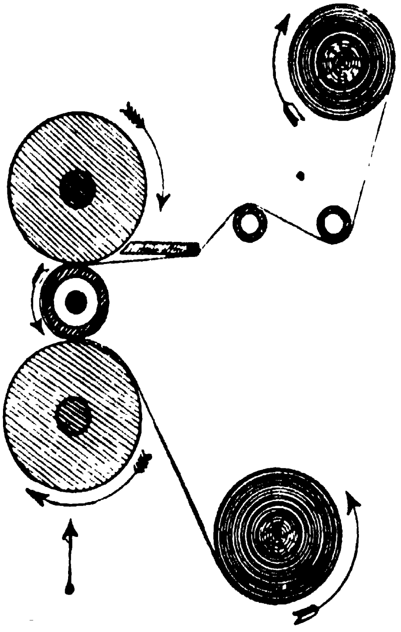

FIG. 44.

and brushed, to remove the cut fly, and are then finished—if to be left white—or dyed, printed, etc.

Damping follows starching and drying, in order to fit the goods for the subsequent treatment, the fibres lacking the requisite flexibility when dry. The damping machine employed for this purpose consists chiefly of a quick-running brush, partly immersed in a trough of water, which is thus discharged, in the form of a fine spray, on to the goods as they are drawn by. A screen of fine gauze is interposed between the brush and the goods in order to keep back large drops of water, which would otherwise render the damping irregular.

Goods intended for stiff finish are not put through any further finishing process, properly so-called; but those required to exhibit softness and lustre are next calendered. The calendering machines used, for the most part, consist of three superimposed rollers, subjected to heavy pressure, the middle roller being of steel, and the other two of paper (Fig. 44), by pressing a number of layers of very good class paper upon steel cores. The use of steel rollers throughout would be calculated to damage the fibre under the heavy pressures employed. According to the effect desired, the goods in the calender may be fed either between two of the cylinders or all three. This treatment breaks up the cohesion of the dressing preparation, and imparts softness and gloss to the fabric. Hot calendering gives a better gloss, and therefore the steel cylinder is provided with a steam-heating arrangement. To obtain the highest degree of gloss, the goods are put through the friction calender, which has two steel cylinders and an intermediate paper one, the friction being produced by running one of the steel cylinders faster than the other. The effect is sometimes heightened by giving the steel cylinder a lateral motion as well. If a single passage through the machine does not produce the desired result the operation is repeated. Calendering machines are now made with a larger number of rollers (up to six).

The action of the calender greatly depends on the nature of the dressing preparation employed. Thus, if the fabric be dressed merely with wheat starch, it cannot be raised to any special degree of softness and gloss by repeated calendering, the operation being therefore restricted to crushing the dressing. For glossy finish, use is made of fats, waxes, stearin, etc.

Sometimes unstarched goods are calendered, the object being to make them denser in texture, in order to retard the penetration of the printing colour or the subsequently applied dressing preparation.

Silk-Finish Calender.—In Nommer's calender as made by Kleinwerfer of Crefeld, the metal roller is covered with fine hatching, so that when a fabric is impressed, it acquires a silky sheen. The number of lines ranges from 6 to 25 per millimetre, according to the fabric to be treated, and their inclination toward the axis of the roller also varies from 15° to 45°. This method competes with mercerisation and is largely used for cheap serges (merinos).

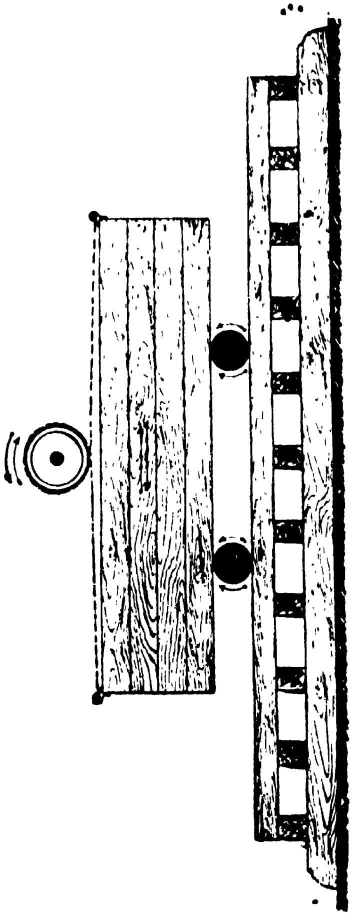

Fig. 45.

A process similar to calendering is that of mangling, which replaces it in some cases. Box-mangles are generally used, consisting of rectangular wooden boxes (Fig. 45) filled with stones and lumps of old iron, and run to and fro over a couple of rollers, on which the fabric to be mangled is wound tightly and without creasing. The goods must be damped in a perfectly uniform manner, since otherwise the fabric might become weakened under the enormous pressure applied. According to the finish in view, the rollers are large or small, and made of wood or metal—large wooden rollers furnishing the best gloss of all. As a rule, the goods are left in the mangle during four to six double traverses of the weighted box. In another type

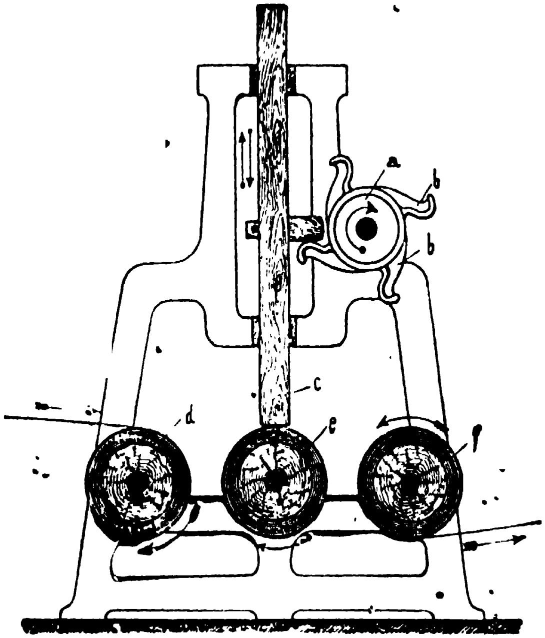

FIG. 46.

of mangle the roll of cloth is rotated under powerful pressure, between two heavy metal rollers.

Beetling is a stamping process which produces an atlas-like gloss. The goods are wound on a wooden roller, covered with calico and situated underneath a row of wooden stamps actuated by lifting cams (Fig. 46). There are usually two pieces in a length, and three lengths side by side on each roller.

In the section shown in the drawing, the lifting cams are represented by *b*, and are mounted, spirally, on the shaft *a*; *c* is one of the wooden stamps; *e* is the full roller in the machine; *d*, one that is finished, and *f*, one filled with cloth ready for insertion in the machine.

The rollers revolve at slow speed, and at the same time are moved to and fro longitudinally. After being beetled for about half an hour, the goods are taken out, wound on another similar roller, and put through the same treatment over again.

In the new Mather and Platt beetles, the wooden stamps are fastened to metallic springs and are much more productive than the older form. They have not yet, however, been able to entirely displace the older machines, the latter furnishing better results in point of quality.

Some fabrics are moiréd or stamped.

Moiré or watered effects are optical effects produced by compressing some parts of the threads flat, and leaving the remainder in their natural condition, thus producing the impression of a pattern.

Various methods are employed for this purpose—

1. By running the fabric double through the calender;
2. By mangling;
3. By calendering between two rollers, one of which is smooth, the other engraved with a large number of mutually intersecting lines. A lateral movement is also imparted during the rotation;
4. The fabric is subjected to the action of an engraved roller bearing a moiré design.

Soft fabrics alone are suitable for this process, and consequently fatty dressing preparations are employed.

Stamping consists in producing a raised design by the aid of an engraved roller, and can therefore only be practised on soft-finish goods. A three-cylinder calender is employed, the middle one being of metal and engraved, the two others of paper.

Some goods finished with fatty dressings are also lustred or glossed by ironing with a steel iron.

The final operations in finishing cotton goods consist of folding, lapping, measuring, and pressing, each effected by the aid of special appliances. Pressing, the object of which is to reduce bulk, is mostly performed in hydraulic presses where a large number of pieces, arranged side by side, piled one row on another, and separated by plates of zinc or boards, are treated at one operation.

The selection and performance of the foregoing operations in the finishing process depend on the quality of the goods, and may differ considerably. Some white goods are not dressed at all, but are simply damped and calendered hot (so-called "natural finish"). Hard finish is produced by merely starching and drying, and "half smooth" finish by a second calendering, etc.

Raised goods (flannels, fustian, calmuck, etc.) require a special treatment to produce a soft nap or pile on one or both sides of the stuff. This is effected in the raising machine, which mainly consists of horizontal cylinders arranged in a semicircle and fitted with a number of steel points. One part of the set is moved in one direction, the rest in the opposite direction. The goods to be raised must be perfectly dry. Raising is applied to both white and coloured or printed goods; in the latter cases the raising may be effected before or after dyeing or printing.

Raised cotton goods of this kind serve as cheap imitations of woollen goods.

Linens are finished in just the same manner as cottons. In this class of goods the beetling process plays a very important part, and imparts to these fabrics their highly prized gloss. Linens are not put through the raising process.

Hemp and jute goods are generally calendered under heavy pressure, in order to press the threads out flat, and thus give the fabric a closer appearance.

The finishing of silk goods resembles that of cottons, inasmuch as the same operations, or nearly so, are employed in both cases. However, as stated in the introduction, silken fabrics are rarely stiffened with dressing preparations; and these, when used at all, are of very simple constitution, containing nothing but gum, dextrin, or size.

Each separate quality and kind of fabric requires special treatment. As a rule, the fabric, on leaving the loom, is cleaned by means of steel roller brushes, then shorn or gassed, rubbed with smoothly polished steel plates to straighten out the threads, and eventually coated, while in a stretched condition, with dressing preparation, applied on the back; then dried and pressed or calendered. Properly woven silk goods are mostly only warm pressed after the projecting fibres have been removed and the threads straightened out and stopped. The pressing is effected either in the press, with hot plates, or in the calender. The finest silks are merely smoothened by cold pressing. These fabrics are neither raised, beetled, nor mangled.

Finishing Woollens.—Woollen fabrics are put through a more complex finishing process than any other kind of textile goods. The methods employed depend on whether the fabric belongs to the woollen or the worsted class. In either case a large number of operations have to be gone through, according to the quality, etc., and these consist of various mechanical treatments, the application of dressing preparations being seldom resorted to.

Of the operations already described, those of beetling, mangling, moiréing, and relief-stamping are never applied to woollens; and the other processes of stenting, shearing, raising, and pressing are performed in a different manner from that practised in the case of cottons.

Shearing is effected in special shearing machines. Raising is an important operation, especially in the case of woollen cloths. It consists in loosening the surface layer of felt and laying the wool fibres in the form of a nap. This is done in the raising gig, the working part of which consists of a drum covered with rows of teazles or card clothing. Dull carding pins are used at first to raise the fibres out of the fabric slowly and without damage, the sharper pins then laying the fibres smoothly in the one direction.

The fabric must be raised in a damp state, since when dry the fibres are not sufficiently supple, and are liable to injury during the process. On the other hand, the fabric must not be too wet, or the carding pins will become too soft. The longer the cloth is raised in a semi-wet state, the better the gloss and the more firmly will the nap be stroked down on the surface.

Pressing is a far more important operation in the finishing of woollen goods than in any other fabrics, and is performed in a special manner for each different class of material. Hot pressing alone is given, since it is only by heat (or moisture) that the wool hairs are rendered flexible. Hydraulic presses are generally used, the goods being piled up, a number of pieces together, with hot metal sheets between each two pieces, and layers of millboard between the separate folds of the cloth. In some places the heating is effected by enclosing the press in a heating chamber. The modifications of this operation consist in differences of duration and degree of pressure applied, the greatest lustre being obtained by prolonged exposure to heavy pressure. To produce high lustre the cloth is pressed several times under heavy pressure and for some hours at a time, being often left in the press all night. The pressure is applied lightly at first and increased afterwards. Some woollens are pressed for only a few minutes, the object in such cases being merely to smooth them out without producing any lustre.

A variety of continuous pressing, usually employed as a preparation for the actual process, is effected on the trough press, a machine consisting of a trough-shaped metal plate in which a metal cylinder slowly revolves, both being heated. The fabric passes slowly between the cylinder and the plate, and is thereby gently pressed and smoothed.

The finishing of woollens also comprises three operations that are unknown in the finishing of other fabrics, *viz.* steaming, crabbing, and fulling or milling.

The steaming process is also known as "decatiring," from an old French word meaning to deprive of lustre, though, as a matter of fact, this sense of the word is only applicable to one modification of the process, namely, the removal of the greasy lustre produced on woollen cloth by pressing, the pile of the cloth being caused to stand up a little by passing the fabric over an arched plate of perforated metal through which a current of steam is being passed.

In the process of steaming, properly so-called, the fabric is wound tightly around a perforated metal cylinder, through the axis of which steam is admitted to the interior. The steam may be caused to pass through the material from the inside, or *vice versa*.

In the former case (the old method) the steam enters through the axis of the cylinder; in the other (vacuum steaming) the cylinder is placed in a closed casing into which steam is admitted, and is drawn through the material into the cylinder and discharged outside.

Steaming softens the fibres and fixes the several layers in the fabric in the position imparted to them by pressing. The more tightly the fabric is wound on the cylinder, and the longer it is steamed, the higher the lustre.

Some articles are steamed for a long time, and then left to cool down before being unrolled from the cylinder; others, again, are steamed for only a few minutes, and immediately unwound; from which it is evident that, like pressing, this operation can be performed in a variety of ways.

In other cases, again, the goods on the steaming cylinder are immersed in a vat or chest into which steam is admitted, *i.e.* steam is applied to both sides of the goods at once.

Crabbing or potting is a mild form of steaming applied chiefly to half-wool and light woollen goods. In this operation the goods are more or less tightly wound on a roller, which revolves in a vessel of hot water. This treatment softens the pile and fixes it in its existing position, with the result that the subsequent displacement likely to occur, owing to different degrees of hygroscopicity in the fibres of these mixed fabrics is retarded.

Fulling or milling is principally employed in the production of woollen cloth, and is an operation based on the felting capacity of wool fibre. In performing this treatment, the woollen fabric is fastened end for end like a sack, and impregnated with a solution of soap in a fulling mill (see Fig. 47), where it is left for some considerable time.

The fulling mill consists chiefly of two adjustable rollers, a_1, a_2, through which the material is passed in its full breadth; c_1, c_2 are the real milling rollers; *d* is a conduit in which the goods are pressed into folds; *e* is the flap closing the outlet of same, and *f* the spring acting on this flap.

Fig. 47 also shows the feed conduit, *b*; the band of cloth, *g*; a perforated board, *h*, which tips up when a knot occurs in the band, and thus stops the machine; *i* is a flap through which the fulling liquor is introduced, and *k* is the door.

The effect of the milling process is in direct relation to the length of exposure, and also depends on the setting of the aforesaid rollers. Thus, for example, a piece of cloth 50 yards long can be milled until the length has shrunk to 30 yards; again, military blankets can be shrunk from their original dimensions of 11½ feet by 82 inches to 5 feet by 65 inches in about four hours.

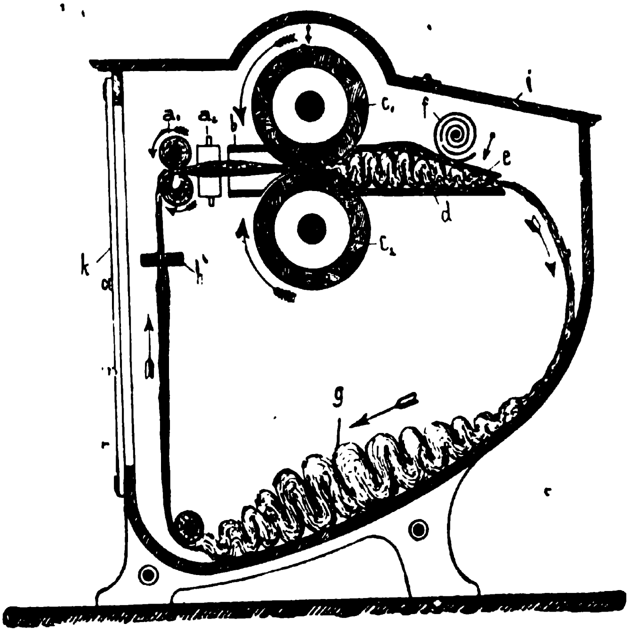

FIG. 47.

Slight milling is also applied to some worsted fabrics, and even to mixed fabrics, special effects being often produced by this means.

The process known as "impregnation" is often combined with milling, and consists of incorporating shorn hairs with the fabric by adding to the latter in the fulling mill as much as

20 to 25 per cent., and sometimes up to 70 to 80 per cent. of its own weight of the pile hairs obtained by shearing the cloth. These are applied to the underside of the material, with which they become incorporated, thanks to the felting property of the fibres.

Much has been written and discussed of late respecting the acid process of milling, wherein the soap solution is replaced by sulphuric acid. Up to the present, however, the method has only given good results in the manufacture of felt.

Finally, a process of curling is employed, chiefly for the purpose of imparting a curly appearance to the surface of winter overcoatings. In this process a plate, fitted with a brush, is pressed on the damped cloth, and set in motion in various ways, mostly rotatory, the motion influencing the style of curl produced.

The complex character of the finishing process applied to woollen fabrics may be gathered from the following summary of the operations comprised in two very common modes of finishing:—

1. A smooth, so-called "Oriental" cloth, on issuing from the loom, is first washed with soda, then milled, carbonised, raised twice, stented, shorn, passed through the trough press, pressed in the hydraulic press, and steamed. Up to this point it is immaterial whether the stuff has been dyed in the wool or will be in the piece, but from this stage onward their treatment is different, piece-dyed goods being then dyed, washed, dried on the stenting frame, shorn, and (generally) pressed thrice. Wool-dyed goods are damped, raised, shorn, pressed, steamed, and pressed twice.

2. Worsteds are mostly nopped, washed with soap and soda, dried, gassed, brushed, gassed, damped, steamed, stented, dyed, washed, crabbed, stented, shorn, pressed, steamed, and pressed again.

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